Controlled Synthesis and Chemical Design of Cuprous Delafossite Oxides for Energy Conversion and Catalysis

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Thomas I. Draskovic

Graduate Program in Chemistry

The Ohio State University

2016

Dissertation Committee:

Prof. Yijing Wu, Advisor

Prof. Anne C. Co

Prof. Patrick M. Woodward
Abstract

Cuprous delafossite oxides are a family of copper-based complex oxides uniquely structured with alternating layers of linearly coordinated O-Cu\textsuperscript{I}-O and M\textsuperscript{III}O\textsubscript{6} edge-shared octahedra. This structure is responsible for several interesting properties, such as p-type conductivity through a delocalized Cu 3\textit{d}- and O 2\textit{p}- orbital valence band, susceptibility to both extrinsic acceptor doping and oxygen intercalation, and high optical transparency. However, reported applications of these oxides have been relatively limited, especially compared to perovskite-structured oxides. One reason for this is likely the difficulties faced controlling morphology, impurities, and doping in their syntheses. The work presented here starts with this synthetic challenge, first focusing on the synthetic chemistry in understanding the phase formation and crystallization of CuScO\textsubscript{2}, then from the observed properties of CuScO\textsubscript{2}, the potential application of delafossite oxide as oxygen electrocatalysts is proposed and investigated.

The properties of CuScO\textsubscript{2}, a potential p-type transparent conducting oxide, lead to several synthetic challenges. Significant oxygen intercalation within copper layer means control of oxidation proves difficult by the conventional solid state syntheses. Through consideration of copper and scandium species hydrolysis, the first hydrothermally synthesized pure-phase CuScO\textsubscript{2} is reported. Post-annealing treatments were used to investigate the influence of oxygen intercalation and were found to increase copper oxidation, leading to increased light absorption, and flat-band potential shifts.
The observed oxygen intercalation in CuScO$_2$ led to an original research proposal and subsequent demonstration of cuprous delafossite oxides as catalysts for the alkaline oxygen reduction reaction. The delafossite structure possesses several key elements that could potentially make it desirable for ORR catalytic applications: the presence of low-coordination Cu-sites, accessible by O$_2$ molecules, and the ability to alter lattice space around Cu-sites by changing the size of the M$^{III}$ cation. CuLaO$_2$ was found to have the most prevalent complete reduction of oxygen out the oxides tested.

Finally, preliminary studies on the use of CuLaO$_{2+x}$ as a potential low temperature solid oxide fuel cell cathode material for low temperature oxygen reduction are presented. The experimental setup and custom fabricated cell holder are detailed, followed by electrochemical impedance spectroscopy tests to compare the oxide to commercially available cathode materials. The CuLaO$_{2+x}$ phase shows potential at very low temperature ($< 400 \, ^\circ\text{C}$), and promising new directions are discussed.

Cuprous delafossite oxides provide a unique framework for tuning chemical and catalytic properties. Focus on individual copper and scandium species hydrolysis led to the first reported phase-pure CuScO$_2$ hydrothermal synthesis. The presented rationale can be applied to other delafossite oxides, allowing for improved morphology and doping control. The first demonstration of cuprous delafossite oxides as alkaline oxygen reduction catalysts and investigation of their low temperature catalytic properties show the potential for tunable copper sites in a variety electrocatalytic processes involving oxygen species.
Acknowledgments

The work presented here would not have been possible without the help and support of the Ohio State University Department of Chemistry and Biochemistry. Particularly, I would like to thank my advisor, Prof. Yiyeng Wu, for his mentorship, motivation, and patience in my research. Also, I thank the past and present members of the Wu group for their discussions, suggestions, and assistance in experiments. Drs. Mingzhe Yu and Zhongjie Huang helped me get started in the group and were inspiring senior graduate students.

Finally, I thank my parents for their love and support throughout all of my education, and my older brother for his insights as a fellow graduate student and endless discussions on everything from science and politics to music and cycling.
Vita

2011..............................................................B.S. Chemistry, Penn State University

2011 to present ........................................Graduate Research Associate, Department

of Chemistry and Biochemistry, The Ohio

State University

Publications of Graduate Study

Draskovic, T.I.; Yu, M.; Wu, Y. “2H-CuSeO$_2$ Prepared by Low-Temperature
Hydrothermal Methods and Post-Annealing Effects on Optical and Photoelectrochemical

Yu, M.; Draskovic, T.I.; Wu, Y. “Understanding the Crystallization Mechanism of
Delafossite CuGaO$_2$ for Controlled Hydrothermal Synthesis of Nanoparticles and

Yu, M.; Draskovic, T.I.; Wu, Y. “Cu (I)-based delafossite compounds as photocathodes
in p-type dye-sensitized solar cells,” Physical Chemistry Chemical Physics, 2014, 16,
5026-5033.

Fields of Study

Major Field: Chemistry
# Table of Contents

Abstract .................................................................................................................................................. ii

Acknowledgments .................................................................................................................................. iv

Vita ........................................................................................................................................................... v

List of Figures .......................................................................................................................................... ix

Chapter 1: Introduction ............................................................................................................................. 1

Chapter 2: 2H-CuScO2 Prepared by Low-Temperature Hydrothermal Methods .................. 5

2.1 Introduction ......................................................................................................................................... 5

2.2 Experimental Methods ....................................................................................................................... 7

2.3 Results and Discussion ....................................................................................................................... 9

Hydrothermal Chemistry and Phase Formation of 2H-CuScO2 ......................................................... 9

CuScO2 Phase Characterization ............................................................................................................. 12

Optical Properties of 2H-CuScO2 Powders ............................................................................................. 16

Copper (I) Oxidation State ....................................................................................................................... 18

2.4 Conclusions ........................................................................................................................................ 21
Chapter 3: Post-Annealing Effects on Optical and Photoelectrochemical Properties of CuScO$_2$ ......................................................... 22

3.1 Introduction .................................................................................. 22

3.2 Experimental ................................................................................ 24

3.3 Results and Discussion ................................................................ 27

Optical Properties of Oxidized 2H-CuScO$_2$ Powders ..................... 27

X-ray Photoelectron Spectroscopy of Oxidized 2H-CuScO$_2$ .......... 29

$E_{fb}$ Measurements of Oxidized 2H-CuScO$_2$ Films ..................... 31

p-Type Semiconductor in Dye-Sensitized Solar Cells ..................... 35

3.4 Conclusion .................................................................................... 37

Chapter 4: Chemical Design of Cuprous Delafossite Oxide Catalysts for Enhanced Oxygen Reduction Activity ................................................................. 39

4.1 Introduction .................................................................................. 39

4.2 Oxygen electrocatalysis ................................................................. 41

4.3 O-Cu$^{1}$-O as Catalytic Centers .................................................. 44

4.4 B$^{III}O_6$ Octahedra as Catalytic Centers ..................................... 49

4.5 Plan of Work .................................................................................. 51

Chapter 5: Cuprous Delafossite Oxides for Alkaline Oxygen Electro catalysis ................................................................. 52

5.1 Introduction .................................................................................. 52
5.2 Experimental ........................................................................................................ 55

5.3 Results/Discussion ............................................................................................... 57

Influence of Cu-Cu Distances .................................................................................. 57

Influence of CuLaO_{2+x} Oxidation ....................................................................... 65

Potential Active B-Site of CuRhO_2 ........................................................................ 70

Delafossite Oxides for Oxygen Evolution Reaction ............................................. 74

5.4 Conclusion .......................................................................................................... 75

Chapter 6: Preliminary Investigation of Oxygen Reduction by CuLaO_{2+x} for Low-
Temperature Solid Oxide Fuel Cell Applications .................................................. 78

6.1 Introduction ....................................................................................................... 78

6.2 Experimental .................................................................................................... 81

6.3 Results and Discussion ..................................................................................... 83

Stable Low-Temperature CuLaO_{2+x} Phase ....................................................... 83

Low Temperature Conductivity of CuLaO_{2+x} .................................................... 89

Solid Oxide Fuel Cell Cathode Symmetric Cell Testing ........................................ 90

6.4 Conclusion and Future Directions .................................................................... 101

Chapter 7: Conclusions .......................................................................................... 104

References ............................................................................................................. 107
List of Figures

Figure 1. PXRD patterns of hydrothermal reaction products with initial reactant pH tuned to 2.0, 5.2 and 10.5. Calculated reference patterns for Cu₂O and ScOOH are shown below................................. 12

Figure 2. Indexed PXRD pattern of hydrothermally synthesized 2H-CuScO₂ with calculated $P6_3/mmc$ reference pattern................................................................. 13

Figure 3. PXRD patterns of solid state synthesized CuScO₂. (a) Cu₂Sc₂O₅ decomposition. (b) CuScO₂ quenching. Calculated reference patterns are given below...................... 14

Figure 4. (a,b) SEM images of CuScO₂ hierarchical clusters. (c,d) Magnified SEM image of cluster edges, highlighting the attachment of smaller plates............................. 15

Figure 5. (a) TEM image of CuScO₂ plate. (b) Corresponding indexed electron diffraction pattern. (c) HRTEM image of CuScO₂ plate edge indicating 120° angle and 2.8 Å lattice spacing viewed along the <001> direction................................................. 16

Figure 6. Kubelka-Munk UV-vis diffuse reflectance spectra of as-synthesized 2H-CuScO₂ (inset: Absorption edge indicating direct optical band gap of 3.52 eV)........... 18

Figure 7. X-ray photoelectron spectra of as-synthesized 2H-CuScO₂. (a) Cu 2p. (b) Sc 2p. ....................................................................................................................... 19

Figure 8. Temperature dependence of the magnetic susceptibility of 2H-CuScO₂ (inset: Inverse susceptibility with linear fit according to the Curie law)........................... 20
Figure 9. (a) Kubelka-Munk UV-vis diffuse reflectance spectra of annealed 2H-CuScO$_2$ samples (inset: corresponding absorption edges). (b) 2H-CuScO$_2$ lattice indicating positions of intercalated oxygen. (c) Digital photographs of annealed samples. 29

Figure 10. Cu 2p X-ray photoelectron spectra of annealed 2H-CuScO$_2$. 30

Figure 11. Cu 2p$_{3/2}$ X-ray photoelectron spectrum of 500 °C Ar, 450 °C air annealed 2H-CuScO$_2$. 31

Figure 12. Chopped-light linear sweep voltammograms (left axes) and photocurrent onset potentials (right axes) of annealed CuScO$_2$ films in aqueous 0.5 M Na$_2$SO$_4$ solution (pH = 12.1). (a) 500 °C Ar, 250 °C Air. (b) 500 °C Ar, 350 °C Air. (c) 500 °C Ar, 450 °C. 33

Figure 13. PXRD patterns of annealed CuScO$_2$ films and after photoelectrochemical (PEC) testing in aqueous 0.5 M Na$_2$SO$_4$ solution (pH = 12.1). All films were annealed at 500 °C in argon prior to indicated air annealing. 34

Figure 14. $I-V$ Curves of annealed CuScO$_2$ films sensitized by the ruthenium-based O18 and the organic PMI$_2$T-TPA dyes using a $I^-/I_3^-$ redox electrolyte. 36

Figure 15. Comparison of typical perovskite and delafossite oxide structures. 40

Figure 16. (a) Variation of the a lattice constant (Cu···Cu distance) with B-site ionic radius. (b) Delafossite structure indicating position of intercalated oxygen; copper (blue spheres), oxygen (red spheres), B-site (green octahedra). 46

Figure 17. Molecular orbital diagrams of end-on and side-on bridged binuclear copper sites. Side-on bridging allows electron density in the $\sigma^*$ orbital of O$_2^{2-}$. 47

Figure 18. Depiction of possible binding modes for dioxygen species with single and binuclear copper sites. 48
Figure 19. PXRD pattern of CuScO$_2$, CuYO$_2$, and CuLaO$_2$. Asterisks (*) indicate peaks solely from the 2H polytypes. .......................................................................................................................... 58

Figure 20. SEM images of solid-state synthesized (a) CuScO$_2$, (b) CuYO$_2$, and (c) CuLaO$_2$. .............................................................................................................................................................................. 58

Figure 21. Cyclic voltammograms of CuScO$_2$, CuYO$_2$, and CuLaO$_2$ thin-film electrodes in argon-saturated 0.1 M KOH. ........................................................................................................................................................................... 59

Figure 22. (a) Rotating-disk linear sweep voltammetry of CuLaO$_2$ in oxygen-saturated 0.1 M KOH. (b) Koutecky-Levich plots of CuScO$_2$, CuYO$_2$, and CuLaO$_2$ at 0.460 V vs. RHE ..................................................................................................................................................................................... 61

Figure 23. Linear sweep voltammograms of CuScO$_2$, CuYO$_2$, CuLaO$_2$, and the carbon black support in oxygen-saturated 0.1 M KOH (Rotation rate: 1600 rpm). ................. 62

Figure 24. (a) Electron transfer number ($n$) and (b) Tafel plots calculated from the Koutecky-Levich equation for RDE data of CuScO$_2$, CuYO$_2$, CuLaO$_2$, and the carbon black support. All potentials were $iR$-corrected. Error bars for electron transfer number represent at least three trials. ........................................................................................................ 64

Figure 25. Linear sweep voltammograms of CuLaO$_2$ without the addition of carbon black, carbon-supported CuLaO$_2$, and the carbon black support in oxygen-saturated 0.1 M KOH (Rotation rate: 1600 rpm). ................................................................. 65

Figure 26. Indexed PXRD patterns and structures showing the differences between the $R$-$3m$ CuLaO$_2$ and $P$-$31c$ CuLaO$_{2-x}$ compounds. .................................................................................................................. 66
Figure 27. (a) Cyclic voltammograms of CuLaO$_2$ and CuLaO$_{2+x}$ thin-film electrodes in argon-saturated 0.1 M KOH. (b) Linear sweep voltammograms in oxygen-saturated 0.1 M KOH (Rotation rate: 1600 rpm). ................................................................. 68

Figure 28. (a) Electron transfer number ($n$) and (b) Tafel plots calculated from the Koutecky-Levich equation for RDE data of CuLaO$_2$, CuLaO$_{2+x}$, and the carbon black support. All potentials were $iR$-corrected. Error bars for electron transfer number represent at least three trials. ........................................................................... 69

Figure 29. XPS Cu 2p spectra of carbon-supported CuLaO$_2$ and CuLaO$_{2+x}$ films. .......... 70

Figure 30. Indexed PXRD pattern of R-3m CuRhO$_2$ with calculated reference pattern (inset: SEM image of CuRhO$_2$ particles). ................................................................. 71

Figure 31. (a) Cyclic voltammograms of CuLaO$_2$ and CuRhO$_2$ thin-film electrodes in argon-saturated 0.1 M KOH. (b) Linear sweep voltammograms in oxygen-saturated 0.1 M KOH (Rotation rate: 1600 rpm). ................................................................. 72

Figure 32. (a) Electron transfer number ($n$) and (b) Tafel plots calculated from the Koutecky-Levich equation for RDE data of CuLaO$_2$, CuRhO$_2$, and the carbon black support. All potentials were $iR$-corrected. Error bars for electron transfer number represent at least three trials. ................................................................. 73

Figure 33. Oxygen evolution response of CuLaO$_2$, CuLaO$_{2+x}$, and CuRhO$_2$ thin-film electrodes in oxygen-saturated 0.1M KOH. Forward and reverse scans were averaged to correct for capacitance. (Rotation rate: 1600 rpm). ................................................................. 75

Figure 34. PXRD pattern of R-3m CuLaO$_2$ before and after low temperature thermal cycling. ......................................................................................................................... 85
Figure 35. Comparison of PXRD patterns for CuLaO$_{2+x}$ and CuLaO$_2$ after low temperature thermal cycling. ........................................................................................................... 86

Figure 36. Indexed PXRD pattern of P-31c CuLaO$_{2+x}$ with calculated reference pattern. ........................................................................................................................................................................... 87

Figure 37. PXRD pattern of P-31c CuLaO$_{2+x}$ before and after low temperature thermal cycling ........................................................................................................................................................................... 88

Figure 38. Thermogravimetric analysis (TGA) of CuLaO$_{2+x}$ under inert (N$_2$) and reducing (5 % H$_2$/95 % N$_2$) atmospheres, indicating $x = 0.63$ (Heating rate = 5 °C min$^{-1}$). .......... 89

Figure 39. (a) Temperature dependent conductivities and (b) corresponding Arrhenius plot of polycrystalline pellets of CuLaO$_2$ and CuLaO$_{2.63}$. ........................................................................................................... 90

Figure 40. SOFC cathode test setup, showing typical cell and custom sample holder..... 91

Figure 41. Nyquist plots of LSM/YSZ/LSM symmetric cell at 400-600 °C in air........ 93

Figure 42. Nyquist plots of CLO/YSZ/CLO symmetric cell at 150-450 °C in air. ....... 94

Figure 43. Nyquist plots of CLO/YSZ/LSM cell at 250-450 °C in air ...................... 95

Figure 44. Nyquist plot comparing LSM and CLO working electrodes on YSZ at 450 °C in air........................................................................................................................................................................... 95

Figure 45. Cross-section SEM images of LSM/YSZ and CLO/YSZ interfaces......... 96

Figure 46. Nyquist plots comparing LSM and LSM-YSZ composite working electrodes at 400-600 °C in air........................................................................................................................................................................... 97

Figure 47. Equivalent circuit model for LSM and LSM-YSZ symmetric cells with fitted values from 450-600 °C ........................................................................................................................................................................... 98
Figure 48. Nyquist plots comparing CLO and CLO-YSZ composite working electrodes at 450 °C in air............................ 99

Figure 49. Nyquist plots of LSM450/YSZ/LSM cell at 400-450 °C in air. LSM450 indicates the LSM electrode annealed at only 450 °C prior to testing............................................. 100

Figure 50. Nyquist plots comparing LSM450 and CLO working electrodes at 450 °C in air. LSM450 indicates LSM electrode annealed at 450 °C prior to testing. ................... 101

Figure 51. Nyquist plots comparing LSM/YSZ/LSM, CLO/YSZ/CLO, and CLO/YSZ/LSM cells at 300 and 350 °C in air. ............................................................. 103
Chapter 1: Introduction

Semiconducting and insulating metal oxides are important classes of functional materials appealing for their tunable compositions which bring diverse structural, chemical, electronic, magnetic and optical properties. In addition, their stability under a wide range of conditions and ease of large-scale fabrication, have allowed metal oxides to be employed in industrial applications such as microelectronic circuits, magnetic memory, electronic displays, photoelectro- and electro-chemical cells, catalysts, and sensors.

The electronic structure of these oxides consists of a valence band and conduction band, separated by a band gap, which is equal to the energy difference between the maximum occupied valence band orbitals and the minimum unoccupied conduction band orbitals. When electrons populate energy levels near the conduction band minimum, the oxide is defined as an n-type semiconductor, and electrons are the majority charge carrier. When these occupied energies are closer to the valence band maximum, the oxide is defined as a p-type semiconductor, and holes are the majority carrier.

To date, the vast majority of researched and applied metal oxide semiconductors are n-type, such as TiO$_2$, ZnO, and SnO$_2$ for coatings, photocatalysis and transparent conducting oxide applications.$^{1-3}$ There are much fewer examples of p-type metal oxides, which is most apparent in the field of transparent conducting oxides, where the n-type
tin-doped indium oxide has dominated applications. Difficulty in obtaining comparable performance to n-type oxides from p-type oxides arises from their electronic band structures. For n-type oxides, electrons are transported through the conduction band, which is typically composed of metal s orbitals. The spatially diffuse s orbitals allow for delocalization of the electrons and low effective masses, thus high mobilities. However, in p-type oxides, the creation of charge carriers (holes) can be difficult itself. Native acceptors, such as cation vacancies that produce holes, have high formation energies relative to native donors, such as anion vacancies that serve as recombination centers for holes. If sufficient hole charge carrier concentrations can be achieved, mobility through the valance band is limited due to the localized nature of oxygen 2p orbitals, which typically form the valance band maximum.

The group of Hideo Hosono first proposed a chemical design strategy for new p-type transparent conducting oxides in the late 1990’s, which they called chemical modulation of the valence band. According to this strategy, the cationic species in metal oxides should have occupied orbitals at comparable energy levels to the oxygen 2p orbitals at the valence band maximum. This would introduce a degree of covalency, hopefully allowing for delocalization of the charge carriers from the oxygen and higher mobility. More specifically for p-type transparent conducting oxides, the cations should also have closed-shell electron configurations \(d^{10}s^0\), \(d^{10}s^2\), or \(d^{10}s^2\) as to eliminate strong coloration caused by d-d transitions. Cu\(^1\)-based oxides fit these requirements, and indeed, Cu\(_2\)O is a well-studied p-type semiconducting oxide, however, it is still strongly colored. Thus, structural consideration may also need to be taken into account to find a suitable
transparent p-type oxide. This led Hosono and coworkers to propose a relatively unstudied family of oxides, the cuprous delafossite oxides, as potential candidates, sparking new interest their synthesis, characterization, and application.\(^6\)

Delafossite, named in honor of the mineralogist Gabriel Delafosse, is a copper iron oxide compound with the formula Cu\(^{II}\)Fe\(^{III}\)O\(_2\). The cuprous delafossite compounds refer to a group of metal oxides which have the same crystal structure as the delafossite CuFeO\(_2\). They have the general formula Cu\(^{I}\)MO\(_2\), where M can be any trivalent cation or even a charge-compensated cation pair maintaining an overall +3 charge.\(^9\) Perhaps most appealing, is the layered structure of monovalent Cu atoms alternating with edge-shared M\(^{III}\)O\(_6\) octahedra. The Cu\(^{I}\) atoms are coordinated to two oxygen atoms with linear O-Cu-O bonds. Each O atom is coordinated with three M\(^{III}\) atoms and one Cu\(^{I}\) atom. The layers can adopt ABCABC or ABABAB stacking, to give the compounds either a rhombohedral (3R) or hexagonal (2H) symmetry.

Benefiting from the crystal structure, the cuprous delafossite compounds are promising p-type transparent conductive oxides.\(^4,6,8\) As mentioned above, the valence band maximum of metal oxides is localized on the O 2p orbitals due to the strong electronegativity of oxygen. Holes at the band edge can be trapped, unable to migrate freely in the lattice, leading to recombination with electrons, and it is therefore difficult for metal oxides to achieve p-type conductivity through acceptor doping. However, in the cuprous delafossite compounds, Cu\(^{I}\) has closed shell 3\(d^10\) orbitals close in energy to the O 2\(p\) orbitals. The similar energies allow for considerable covalency in the interactions, and occupied O 2\(p\)-Cu 3\(d\) antibonding orbitals form the upper valence band maximum. The
hybrid of Cu 3d and O 2p states at the band edge allows for delocalization of charge from the oxygen. Therefore, holes introduced by defects such as Cu vacancies or O interstitials can migrate freely in the valence band edge and the compounds exhibit good p-type conductivity.\textsuperscript{6,9,10} Concerning the optical properties, Cu\textsuperscript{I} has a closed-shell $d^{10}$ configuration, and contrary to Cu$_2$O, the two-dimensional Cu-Cu plane weakens or eliminates d-d orbital interactions.\textsuperscript{11} Hence, the factors that may reduce the band gap are minimized. When this is combined with an M\textsuperscript{III} species with a $d^0$ or $d^{10}$ valence electron configuration (e.g., Al, Ga, In, Sc, Y, La), the resulting compound can be transparent in the visible range, with a large optical band gap (>3.2 eV).

The work detailed in this dissertation, utilizes the delafossite structure and appropriate choice of B-site cations to prepare oxides for photoelectrochemical and electrocatalytic applications. In Chapters 2 and 3, the first pure-phase hydrothermal synthesis of 2H-CuScO$_2$ and its characterization are presented. The choice of scandium allowed for the as-synthesized oxide to be light colored with a wide band-gap due to the $d^0$ configuration. The large ionic radius of Sc\textsuperscript{III} causes sufficient spacing between copper atoms to allow for oxygen interstitial formation and increased charge carrier density. These properties of CuScO$_2$ allowed for its first application as a p-type semiconductor in dye-sensitized solar cells. Chapters 4, 5, and 6 build on the interesting oxygen interstitial formation in certain delafossite oxides by proposing and demonstrating the use of scandium, as well as the larger radii yttrium and lanthanum B-sites, in cuprous delafossite oxides to allow for oxygen electrocatalysis at the copper-site.
Chapter 2: 2H-CuScO\textsubscript{2} Prepared by Low-Temperature Hydrothermal Methods


2.1 Introduction

Delafossite oxides are uniquely structured with alternating layers of linearly coordinated O-Cu\textsuperscript{I}-O and M\textsuperscript{III}O\textsubscript{6} edge-shared octahedra. The layers can adopt ABCABC or ABABAB stacking, to give the compounds either a rhombohedra (3R) or hexagonal (2H) symmetry. CuScO\textsubscript{2} is a particularly interesting member of this family. The valence band consists of Cu\textsuperscript{I} 3d\textsuperscript{10} and O 2p states similar to other delafossite oxides, but the d\textsuperscript{0} nature of Sc\textsuperscript{III} causes significant Sc 3d contributions to the conduction band.\textsuperscript{12–16} These mixed closed-shell orbitals give rise to a direct-allowed band gap determined to be between 3.3 – 3.7 eV based on calculation and experimental data.\textsuperscript{10,15,17,18} Relatively high conductivities are able to be achieved through the susceptibility of CuScO\textsubscript{2} to both extrinsic acceptor doping and oxygen interstitials.\textsuperscript{19} It is the first in a series of delafossite oxides with B-sites of large enough ionic radii to be able to support significant oxygen intercalation within the plane of Cu atoms.\textsuperscript{10,20–22}

Cuprous delafossite oxides present several synthetic challenges. The most obvious being control of copper's oxidation state. Cu\textsuperscript{I} is unstable at high temperatures until above
~900 °C, so temperatures greater than ~900 °C and specific control of heating/cooling rates can be critical in conventional solid state methods. CuScO$_2$ presents an even further challenge due to its ability to allow significant oxygen intercalation within the Cu$^{I}$ layer and be easily oxidized at even low (< 400 °C) temperatures. Typical syntheses for CuScO$_2$ include solid state reaction of the binary components and metathesis reactions, with thin films often prepared by various deposition techniques. In each of these methods, high temperatures, controlled atmospheres, and/or vacuum are required to produce light colored, pure 3R or 2H CuScO$_2$ with minimal oxidation. More recent synthetic studies of CuScO$_2$ performed by the Poeppelmeier group improved upon earlier hydrothermal syntheses of several delafossite oxides by using a hydrothermal Teflon-pouch method. This method allowed for low temperatures (< 210 °C), control over hydrolysis of the reactants, and could be applied to many delafossite compounds.

The following reaction was attempted at 210 °C for 60 hours with 2.5 M NaOH:

$$\text{Cu}_2\text{O} \ (s) + 2 \text{Sc(OH)}_3 \ (s) \rightarrow 2 \text{CuScO}_2 \ (2H, 3R) + 3 \text{H}_2\text{O} \ (l)$$

However, consistent with previous solid state syntheses, pure 2H or 3R phase was difficult to achieve and only a mixed 2H, 3R sample was obtained. Sample washing with dilute acid was also necessary to remove ScOOH impurities.

In this chapter, the hydrothermal synthesis of CuScO$_2$ was reexamined using a modified ethylene glycol-assisted hydrothermal synthesis. Through consideration and careful control of the hydrolysis of Cu$^{I}$ and Sc$^{III}$ species, a pure, single hexagonal polytype CuScO$_2$ was obtained. Large surface area, hierarchical structures were formed, and the as-synthesized beige powder had minimal oxidation of the Cu$^{I}$. The reported
hydrothermal synthesis provides future opportunities for extrinsic acceptor doping to increase conductivity and the potential for morphology control.

2.2 Experimental Methods

Materials. Copper (II) nitrate (hemi)pentahydrate (98.0%, Sigma-Aldrich), scandium (III) nitrate hydrate (99.9%, Sigma-Aldrich), copper (I) oxide (97%, Sigma-Aldrich), copper (II) oxide (98%, Sigma-Aldrich), scandium (III) oxide (99.9% Sigma-Aldrich), potassium hydroxide (90%, Sigma Aldrich); ethylene glycol (99.0%, Sigma-Aldrich), de-ionized water ($\rho = 18$ M$\Omega$cm, Barnstead E-Pure), aqueous ammonia solution (29.0%, Fisher Scientific), and argon (99.998%, Praxair, Inc.) were used without further purification.

Hydrothermal Synthesis. A modified hydrothermal synthesis was used for CuScO$_2$ based on previous literature.$^{34}$ Equimolar amounts of copper and scandium nitrates (5 mmol) were dissolved in deionized water and 3 mL ethylene glycol. The pH of the solution was adjusted to 3.2 using KOH. The final solution, with a volume of 13.8 mL, was placed in a 23 mL Teflon-lined stainless steel autoclave (Parr Instrument Company). The sealed autoclaves were heated at 210 °C for 60 hours. After reaction, the precipitates were collected by centrifugation and washed several times with water. If necessary, dilute ammonium hydroxide was used to remove any copper impurities. The powders were dried overnight at 60 °C in a vacuum oven before characterization.

Solid State Synthesis. Following previous literature reports, typical solid state syntheses of CuScO$_2$ were performed. The first route involved synthesis of Cu$_2$Sc$_2$O$_5$ by the heating of CuO and Sc$_2$O$_3$ at 1000 °C in air for 24 hours. The Cu$_2$Sc$_2$O$_5$ phase was then reduced
to CuScO$_2$ under argon at 1050 °C for 36 hours.$^{22,26}$ The second route involved a direct reaction between Cu$_2$O and Sc$_2$O$_3$ at 1100 °C in air for 24 hours. A pressed pellet of the reactant powders was buried in small amount of sacrificial powder and the reaction was quench-cooled in air to avoid decomposition.$^{35}$

**Characterization Methods.** Products were characterized by powder X-ray diffraction (PXRD) with a Rigaku Corp. Geigerflex using Cu Kα$_1$ radiation. Lattice parameters were refined using the CELREF software.$^{36}$ Scanning electron microscopy (SEM) images were obtained with an FEI/Philips Sirion Field Emission SEM. Transmission electron microscopy (TEM) images and selected-area diffraction patterns were obtained with an FEI/Philips CM-200, whereas high-resolution TEM (HRTEM) images were obtained with an FEI Titan$^{3}$™. For TEM, the sample powder was dispersed in isopropanol and dropped on a Au grid; small plate fragments from the sample were imaged. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were collected on a Perkin-Elmer Lambda 950 spectrophotometer with a 60 mm integrating sphere and a Spectralon® reflectance standard. X-ray photoelectron spectroscopy (XPS) characterization was performed with a Kratos Axis Ultra XPS spectrometer using monochromatic Al Kα radiation at an operating voltage of 12 kV and a current of 10 mA. The sample powder was pressed onto carbon tape on the sample holder, and an electron flood gun was used to avoid surface charging problems. Spectra fitting was performed with the CasaXPS software according to previously reported parameters, using combined Gaussian–Lorentzian profiles with a Shirley-type background.$^{37}$ Temperature dependent magnetic moment measurements were performed using a Quantum Design Magnetic Property Measurement System.
(MPMS) superconducting quantum interference device (SQUID) magnetometer. The $\chi_{\text{mol}}$ values were corrected by subtraction of the core diamagnetism of the relevant ions.\textsuperscript{38}

2.3 Results and Discussion

Hydrothermal Chemistry and Phase Formation of 2H-CuScO$_2$

Hydrothermal synthesis of complex oxides presents a challenge, in that the hydrolysis and oxidation state of two or more metal species must be controlled. Thus, it is difficult to find a universal set of synthetic conditions that can be applied to oxides even of the same family.\textsuperscript{32,33} The Poeppelmeier group's "Teflon pouch method" was successfully applied to many delafossite oxides, but CuScO$_2$ yielded mixed 2H, 3R polytypes.\textsuperscript{32,33} A high base concentration was necessary to dissolve any appreciable amount of the Sc(OH)$_3$ reactant, and solubility of Cu\textsuperscript{I} species suffers under these alkaline conditions. Due to this, the products still contained unreacted ScOOH in addition to the mixed polytype CuScO$_2$. In attempt to produce phase pure CuScO$_2$, ethylene glycol assisted\textsuperscript{32} hydrothermal reactions were modified, considering the hydrolysis of both copper and scandium.

Consideration of Cu\textsuperscript{I} hydrolysis. The Pourbaix diagram for copper was referenced to approximate stable hydrothermal conditions for Cu\textsuperscript{I} species.\textsuperscript{39} At room temperature, Cu\textsuperscript{I} is not stable at any pH in aqueous solution, easily disproportionating into Cu\textsuperscript{0} and Cu\textsuperscript{II}. Increasing temperature expands a wider stable pH region for Cu\textsuperscript{I}, and at 200 °C, the dominant species will be Cu\textsuperscript{I} (aq) when the pH < ~6.8. Above this pH, the stable Cu(OH) (aq) has low solubility ($\sim$10$^{-3}$–10$^{-4}$ mM) and easily precipitated as Cu$_2$O. The presence of
soluble alcohols (ethylene glycol, ethanol, isopropanol, etc.), which are capable of acting as reducing agents, also further stabilizes Cu\(^{\text{I}}\) as follows:

\[
(CH_2OH)_2 (l) \xrightarrow{\Delta} CH_3CHO (l) + H_2O (l)
\]

\[
2CH_3CHO (l) + 2Cu^{\text{II}} (aq) \rightarrow (CH_3CO)_2 (l) + 2Cu^{\text{I}} (aq) + 2H^+ (aq)
\]

Ethylene glycol is believed to be thermally decomposed to acetaldehyde, which in turn reduces the copper species, producing diacetyl.\(^{40}\)

*Consideration of Sc\(^{\text{III}}\) hydrolysis.* Studies on the aqueous geochemistry of metal species are also valuable resources for approximating their behavior under laboratory hydrothermal reaction conditions.\(^{41}\) At saturated water vapor pressure and typical hydrothermal reaction temperatures of 200–300 °C, Sc(OH)\(_2^+\) (aq) is the dominant species in a very narrow range from pH ≈ 3–3.5, then Sc(OH)\(_3^0\) (aq) within the broader range of pH ≈ 3.5–7. Considering stability of Cu\(^{\text{I}}\), a pH range of 3–6 should be appropriate for formation of CuScO\(_2\). However, under weak acidic conditions, Sc(OH)\(_3^0\) can precipitate as the stable ScOOH:

\[
Sc(OH)_3^0 (aq) \rightarrow ScOOH (s) + H_2O (l)
\]

Due to the broad solubility minimum of ScOOH, moderate acidic conditions should be suitable for the transport of Sc species and reduce unreacted hydroxide impurities.

*Hydrothermal Synthetic Conditions.* With a better understanding of the hydrothermal chemistry of copper and scandium, synthetic conditions could be established for CuScO\(_2\). Numerous reactions were attempted with pH adjusted from 2 to 11. Indeed, it was found that only in a narrow range around pH = 3.2 significant formation of CuScO\(_2\) occurred. Above this pH, ScOOH would dominate, and attempts at dissolving the impurity with
dilute acid also led to dissolution of the CuScO$_2$. Below this pH, various broad diffraction peaks appeared that could not be matched to any particular copper or scandium compounds but were likely amorphous hydroxides. Figure 1 shows the powder x-ray diffraction pattern (PXRD) of hydrothermal reaction products with initial pH tuned to 2.0, 5.2, and 10.5. Therefore, at pH = 3.2, Cu$^+$ is stable, there is suitable transport of Sc$^{III}$ species, and product dissolution is avoided. The addition of ethylene glycol has also been shown promote cuprous delafossite phase formation, most likely by acting as a reducing agent and lowering the dielectric constant of the solution.$^{34}$ 3 mL (22% v/v) ethylene glycol was found to best minimize the amount of unreacted ScOOH. Similar to the Teflon pouch method, a temperature of 210 °C was used to lower dielectric constant of water, and a reaction time of 60 hours ensured full reaction of Cu$^+$ with any poorly soluble ScOOH. The proposed reactions are therefore:

$$\text{Cu}^+ (\text{aq}) + \text{Sc(OH)}_2^+ (\text{aq}) \rightarrow \text{CuScO}_2 (s) + 2\text{H}^+ (\text{aq})$$

$$\text{Cu}^+ (\text{aq}) + \text{Sc(OH)}_3^0 (\text{aq}) \rightarrow \text{CuScO}_2 (s) + \text{H}_2\text{O} (l) + \text{H}^+ (\text{aq})$$
Figure 1. PXRD patterns of hydrothermal reaction products with initial reactant pH tuned to 2.0, 5.2 and 10.5. Calculated reference patterns for Cu$_2$O and ScOOH are shown below.

*CuScO$_2$ Phase Characterization*

To confirm the phase purity of samples, powder X-ray diffraction was performed. Figure 2 shows the diffraction pattern of the CuScO$_2$ obtained from the optimized hydrothermal synthetic conditions. Interestingly, the peaks match well with only with hexagonal $P6_3/mmc$ polytype, with no evidence of the peak broadening can occur from stacking faults in mixed rhombohedral (3R) and hexagonal (2H) samples.$^{26}$ The refined lattice parameters $a = 3.218(6)$ Å, $c = 11.384(1)$ Å also match those previously reported for hexagonal sample prepared by solid state methods.$^{10,25,26}$ Although careful tuning of pH is required, the reported hydrothermal method can repeatedly produce pure 2H-CuScO$_2$. 

12
The formation of a pure 2H product is significant considering the great difficulty faced in other synthetic methods. Solid state syntheses have required controlled atmospheres, quenching of the reactions from high temperatures, and/or extrinsic doping to stabilize the 2H polytype; Exchange reactions between LiScO$_2$ and CuCl have yielded pure 3R-CuScO$_2$ but require careful handling of CuCl and sealing of evacuated quartz tubes.\textsuperscript{10,25,26,28} For comparison, Figure 3 shows the PXRD patterns of CuScO$_2$ synthesized by two common solid state routes. The first procedure required the formation of an intermediate Cu$_2$Sc$_2$O$_5$ phase (Figure 3a), whereas in the second, the reaction had to be quenched from an 1100 °C furnace (Figure 3b). Yet still, neither reaction produced a pure polytype. Cu$_2$Sc$_2$O$_5$ decomposition led to a majority R-3m, whereas the direct quenched reaction yielded a more equal mixture of both rhombohedral R-3m and hexagonal P6$_3$/mmc. Aside from controlling the polytype formation, obtaining any delafossite phase by the solid state methods can prove challenging due to the relative stability of Cu$_2$O and M$^{III2}$O$_3$ at lower temperatures, as detailed in a recent study.\textsuperscript{24}
Figure 3. PXRD patterns of solid state synthesized CuScO$_2$. (a) Cu$_2$Sc$_2$O$_5$ decomposition. (b) CuScO$_2$ quenching. Calculated reference patterns are given below.

The product morphology of the hydrothermal 2H-CuScO$_2$ was characterized by SEM, as shown in Figure 4. Large hierarchical clusters of plates with diameters from 5 to 10 μm were formed. Similar large clusters, designated as “gypsum flower,” were also observed at low pH conditions in the ethylene glycol-assisted synthesis of CuGaO$_2$, but the exact reason for their formation is not well understood. This structure can also explain the slight broadening of X-ray diffraction peaks containing a c-axis component (i.e. (00$l$) and (h0l)), which is likely due to stacking faults at the intersections of these large plates. Closer inspection of the edges of the plates comprising the large clusters shows the attachment of much smaller plates, indicating that the clusters likely grow by the oriented attachment mechanism of the initially formed small plates. This is promising
for future attempts as smaller particle synthesis through the control and inhibition of the orientated attachment process.\textsuperscript{42}

![Figure 4. (a,b) SEM images of CuScO\textsubscript{2} hierarchical clusters. (c,d) Magnified SEM image of cluster edges, highlighting the attachment of smaller plates.](image)

The smaller plate fragments from the edge of the clusters were isolated for TEM imaging and electron diffraction. Figure 5a,b shows the edge of a clearly hexagonal plate and the indexed selected-area electron diffraction pattern shows the particle's single crystallinity. The HRTEM image of a plate edge shows clear lattice planes with a spacing of $\sim$2.8 Å, closely matching the d-spacing between \{100\} lattice planes. Plates with \{001\} planes exposed on the top/bottom are consistent with previously reported hydrothermally-synthesized 3R- CuGaO\textsubscript{2} and CuCrO\textsubscript{2} particles.\textsuperscript{43,44}
**Optical Properties of 2H-CuScO$_2$ Powders**

One of the unique properties of CuScO$_2$ is that it is the first in a series of cuprous delafossite oxides susceptible to significant oxygen intercalation without decomposition.$^{10,22,28,45}$ The formula of this oxidized compounds is typically written as CuScO$_{2+x}$, with $x$ reaching values up to 0.5.$^{26}$ Controlling oxidation during solid state syntheses has been difficult because this oxidation can occur in air at temperatures as low as 250 °C. Often, a light gray color is obtained, and only in evacuated sealed tubes, can nearly colorless samples be obtained.$^{10,26}$ The 2H-CuScO$_2$ prepared in this work was a light beige color, and XPS indicated initial low levels of oxidation. If desired, the oxidation can now be controlled through post-annealing methods, as discussed in Chapter 3.
UV-vis diffuse reflectance spectroscopy was performed to investigate the optical properties of the freshly prepared CuScO$_2$. Reflectance data was plotted according to the Kubelka–Munk theory:\(^{46}\)

\[ F(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} \]

where \( R_{\infty} \) is the calibrated sample reflectance. The optical band gaps could further be calculated by considering the energy dependence of the absorption coefficient \( \alpha \) near the band gap absorption edge:

\[ \alpha h\nu = (h\nu - E_g)^2 \]

for a direct-allowed transition, where \( \alpha = F(R_{\infty}) \) assuming the sample scattering coefficient remains constant within the narrow energy range of the absorption.\(^{47}\) Figure 6 shows the diffuse reflectance Kubelka-Munk absorption and the absorption edge of the as-synthesized CuScO$_2$. The light beige powder had little absorption in the visible range and was calculated to have a direct-allowed band gap of 3.52 eV. Although optical properties of bulk powder CuScO$_2$ samples have not been studied, the determined band gap is consistent with previous calculations and experimental data from thin films.\(^{10,15,17,18}\) Explanations for the increased absorption around 375–500 nm include the possibility for a broad distribution of surface state energy levels and more simply, the possible reflection of light within the hierarchical clusters resulting in a longer optical path length and greater absorption.
Figure 6. Kubelka-Munk UV-vis diffuse reflectance spectra of as-synthesized 2H-CuScO₂ (inset: Absorption edge indicating direct optical band gap of 3.52 eV).

Copper (I) Oxidation State

XPS was performed on the as-synthesized CuScO₂ to verify the chemical states of copper and scandium. Figure 7 provides the spectra at binding energies corresponding to Cu 2p and Sc 2p. The Cu 2p spectrum indicates a Cu 2p₃/₂ peak at 932.7 eV and a Cu 2p₁/₂ peak at 952.5 eV. The peak regions were fit well by one component, and the binding energies are consistent with those for Cu¹ oxides.³⁷,⁴⁸ The Sc 2p spectrum indicates a Sc 2p₃/₂ peak at 401.5 eV and a Sc 2p₁/₂ peak at 406.0 eV, matching with those previously reported for Sc₂O₃.³⁷,⁴⁸ Although the peaks could not be fit clearly by single components, attempts to fit with more components did not provide any improvement. Possible explanations for this include a small amount of surface charging or the presence of surface hydroxide groups. Despite this, the Sc 2p spectra were consistent across several samples.
To further probe the low oxidation of the as-synthesized 2H-CuScO\(_2\), temperature dependent magnetic susceptibility measurements were performed. The copper (I) ion has a filled inner shell (3\(d^{10}\)), so stoichiometric CuScO\(_2\) is expected to be diamagnetic. However, the presence of copper (II) with one unpaired electron (3\(d^{9}\)) can introduce a paramagnetic response in an applied field. Figure 8 shows the magnetic susceptibility curve from 2.8 – 300 K.
As expected, across the majority of the temperature range (> 100 K), a diamagnetic response was observed. Diamagnetic materials repel an applied field, giving rise to a negative magnetic susceptibility. At very low temperatures, a small paramagnetic response was observed, possibly due to low temperature ordering of small amounts of copper (II) ions or rare-earth impurities. When fitted to the Curie law (shown in inset) the response yields an effective magnetic moment of 0.16 $\mu_B$. This corresponds to only an estimated 0.9 % of oxidized copper present. A similar low temperature response was seen for CuLaO$_2$, also attributed to impurities. The dominant diamagnetic response of the magnetic susceptibility measurements further supports the diffuse reflectance and XPS results, indicating a negligible amount of oxidized copper and a nearly stoichiometric CuScO$_2$. 

![Figure 8. Temperature dependence of the magnetic susceptibility of 2H-CuScO$_2$ (inset: Inverse susceptibility with linear fit according to the Curie law).](image-url)
2.4 Conclusions

CuScO$_2$ was synthesized by low temperature ethylene glycol-assisted hydrothermal techniques. Powder X-ray diffraction and electron diffraction confirmed that the CuScO$_2$ was pure hexagonal P6$_3$/mmc. Reported solid state techniques required precise control of stoichiometry and temperature to obtain pure rhombohedral or hexagonal polytypes, whereas previous hydrothermal techniques have led to mixtures of the hexagonal and rhombohedral polytypes. The as-synthesized hierarchical clusters were light beige in color, showed minimal absorption in the visible range, and XPS indicated no oxidation of the copper sites. The reported hydrothermal synthesis provides future opportunities for extrinsic acceptor doping to increase conductivity and the potential for morphology control.
Chapter 3: Post-Annealing Effects on Optical and Photoelectrochemical Properties of CuScO$_2$


3.1 Introduction

Recent interest in delafossite oxides was spurred by the report of CuAlO$_2$ as a transparent p-type semiconductor with conductivities reaching 1 S cm$^{-1}$. The transparent optical properties of delafossite oxides come from the two-dimensional plane of closed-shell $d^{10}$ Cu$^{1}$, and the choice of an M$^{III}$ species that has that also has a closed-shell $d^0$ or $d^{10}$ valence electron configuration (such as Al$^{III}$), resulting in a large optical band gap (>3.2 eV). The conductivity of CuAlO$_2$ is believed to arise primarily from cation off-stoichiometry (substitution of Cu$^{1}$ by Al$^{III}$). The delafossite CuScO$_2$ also has a large band gap due the $d^0$ Sc$^{III}$, making it suitable for similar transparent semiconductor applications. Also, like other cuprous delafossite oxides, it exhibits p-type conductivity through a small polaron hopping mechanism localized at the copper site. However, a hole mobility of 2.0 x 10$^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$ and conductivities reaching 30 S cm$^{-1}$ have been reported. Relatively high conductivities are able to be achieved through the susceptibility of CuScO$_2$ to both extrinsic acceptor doping and oxygen interstitials.
Delafossite oxides with Sc$^{\text{III}}$ or B-sites of larger ionic radii are able to support significant oxygen intercalation within the plane of Cu atoms.\textsuperscript{10,20–22} For CuScO$_2$, thermogravimetric analysis showed significant mass increases above ~300 °C, with decomposition to Cu$_2$O, CuO, and Sc$_2$O$_3$ at 600 °C.\textsuperscript{26} Rietveld refinement of neutron diffraction data revealed O$^{2-}$ to be in the plane of Cu$^{\text{I}}$. Unfortunately, doping by either an extrinsic acceptor or oxidation darkened CuScO$_2$ samples, with reported colors ranging from white (synthesized in vacuum sealed tube) to dark blue-gray.\textsuperscript{10}

The high conductivities and the potential for transparency in the visible range due to a large band gap with a closed-shell $d^{10}$ Cu$^{\text{I}}$ valence band and Sc$^{\text{III}}$ $d^9$/O $p$ orbital conduction band, make CuScO$_2$ an appealing delafossite candidate for transparent p-n junctions\textsuperscript{51–53} and photovoltaic cathodes.\textsuperscript{43,44,54–61} Important to these application is a synthetic method that could allow for careful control of doping and morphology. Although the synthesis of CuScO$_2$ in Chapter 2 does not provide the typically desired nano-sized particles, the high surface area, hierarchical-structured particles provide a starting point to study the doping and applications of CuScO$_2$. One such potential application, which the Wu group has developed over several years, is p-type dye-sensitized solar cells.\textsuperscript{43,62–72} Even though much of the work was performed on dye synthesis and understanding the performance of cells using p-type NiO as the semiconductor, recently the delafossite CuGaO$_2$ was utilized.\textsuperscript{43} Unfortunately, CuGaO$_2$, similar to CuAlO$_2$, can have limited conductivities. Thus, CuScO$_2$ is a desirable candidate for the semiconductor in p-type dye-sensitized solar cells. Critical to these applications is the influence of annealing temperatures necessary to prepare high quality,
polycrystalline films, particularly because CuScO$_2$ can darken in color and lose transparency when doped.

In this chapter, the hydrothermal synthesis of CuScO$_2$ developed in Chapter 2 is revisited. A series of low temperature annealing steps were performed on polycrystalline films prepared from the hydrothermally synthesized CuScO$_2$ particles. The optical and photoelectrochemical properties of the pure and oxidized product were investigated. Finally, the first p-type dye sensitized solar cell utilizing CuScO$_2$ was assembled and tested.

3.2 Experimental

*Materials.* Copper (II) nitrate (hemi)pentahydrate (98.0%, Sigma-Aldrich), scandium (III) nitrate hydrate (99.9%, Sigma-Aldrich), potassium hydroxide (90%, Sigma Aldrich); ethylene glycol (99.0%, Sigma-Aldrich), lithium iodide (99.9%, Sigma-Aldrich), iodine (99.99%, Sigma-Aldrich), 3-methoxypropionitrile (MPN, Sigma-Aldrich), Triton X-100 (Sigma-Aldrich), H$_2$PtCl$_6$ • xH$_2$O (Sigma- Aldrich), de-ionized water ($\rho = 18$ M$\Omega$•cm, Barnstead E-Pure), aqueous ammonia solution (29.0%, Fisher Scientific), argon (99.998%, Praxair, Inc.), sodium sulfate (99.3%, Fisher Scientific), and sodium hydroxide (98.8%, Fisher Scientific) were used without further purification. The cyclometalated Ru(II) dye complex, O18, was synthesized as described by He *et al.*$^{71}$ The organic donor-acceptor type dye, PMI-T2-TPA, was synthesized as described by Wang *et al.*$^{73,74}$
Hydrothermal Synthesis of 2H-CuScO$_2$. CuScO$_2$ was synthesized as reported in Chapter 2 of this document and in the published literature. No further preparation to the material was performed after synthesis, other than any necessary washing and drying.

Film Preparation. Polycrystalline films of CuScO$_2$ were prepared on fluorine-doped tin oxide (FTO) coated glass slides (TEC 7, Hartford Glass Co., Inc.). The slides were first cleaned by sonication in detergent solution (Decon Contrex® AP), water, ethanol, and acetone, successively. A final 20 minute treatment in an ultraviolet ozone cleaner (Novoscan Technologies, Inc.) was performed. The powders were dispersed in a 1:1 ethanol:water mixture to make a paste, which could then be doctor-bladed on Scotch tape masked FTO slides. After drying at 100 °C, the films were annealed at 500 °C under argon, followed by a final annealing at various temperatures in air to control oxidation of the CuScO$_2$.

Characterization Methods. Products were characterized by powder X-ray diffraction (PXRD) with a Rigaku Corp. Geigerflex using Cu K$\alpha_1$ radiation. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were collected on a Perkin-Elmer Lambda 950 spectrophotometer with a 60 mm integrating sphere and a Spectralon® reflectance standard. X-ray photoelectron spectroscopy (XPS) characterization was performed with a Kratos Axis Ultra XPS spectrometer using monochromatic Al K$\alpha$ radiation at an operating voltage of 12 kV and a current of 10 mA. The sample powder was pressed onto carbon tape on the sample holder, and an electron flood gun was used to avoid surface charging problems. Spectra fitting was performed with the CasaXPS software according to previously reported parameters, using combined Gaussian–Lorentzian profiles with a
Shirley-type background. Temperature dependent magnetic moment measurements were performed using a Quantum Design Magnetic Property Measurement System (MPMS) superconducting quantum interference device (SQUID) magnetometer. The χ_mol values were corrected by subtraction of the core diamagnetism of the relevant ions.38

Photoelectrochemical Cell and Efb Determination. Photoelectrochemical measurements were performed on a Gamry Instruments Reference 600 potentiostat. A 435 W Xe lamp with a water IR-filter (Oriel) was used to illuminate the samples with a chopping frequency of 0.05 Hz and a scan rate of ν = 1 mV/s. An aqueous 0.5 M Na2SO4 electrolyte solution was adjusted to the desired pH with NaOH. The reference electrode was a Ag/AgCl (sat. KCl) electrode and platinum mesh was used as the counter electrode. The working electrode was a CuScO2 film on FTO-coated glass. All solutions were purged with argon for at least 30 min before the experiments. Samples were illuminated from the back side.

Solar Cell Fabrication and Measurement. CuScO2 films were fabricated with a CuScO2 “paste.” The typical paste was made by adding 30μL 0.6% (v/v) acetic acid and 30μL 1% (v/v) Triton X-100 polymer in isopropanol as surfactant into a CuScO2 aqueous dispersion to give the desired consistency. The paste was then doctor-bladed on Scotch tape masked FTO slides. FTO glass slides were previously cleaned as described above. After drying at 100 °C, the films were annealed at various temperatures in air to remove any solvent/polymer, followed by an annealing at 500 °C under argon. Annealing times were 30 minutes.
The dye sensitization was accomplished by immersing the films into a 0.14 mM O18 dye in dry acetonitrile solution for approximately 16 hours. Counter electrodes were prepared via the thermal deposition of a H$_2$PtCl$_6$ solution at 385 °C for 20 min. The sensitized CuScO$_2$ working and Pt counter electrodes were assembled by heating with a Surlyn® 60 μm film (Solaronix). The electrolyte solution (0.1 M I$_2$/1 M LiI in MPN) was filled from a predrilled hole in the counter electrode via the vacuum back-filling technique. The $J$–$V$ curves were recorded under 100 mW cm$^{-2}$ AM 1.5 illumination generated by a solar simulator (Small-Area Class B, Solar Simulator, PV Measurements, Inc.).

3.3 Results and Discussion

Optical Properties of Oxidized 2H-CuScO$_2$ Powders

One of the unique properties of CuScO$_2$ is that it is the first in a series of cuprous delafossite oxides susceptible to significant oxygen intercalation without decomposition.$^{10,22,28,45}$ The formula of this oxidized compounds is typically written as CuScO$_{2+x}$ ($x \leq 0.5$), with oxidation occurring in air at temperatures as low as 250 °C.$^{26}$ Thus, controlling oxidation during solid state syntheses has been difficult. Often, a light gray color is obtained, and only in evacuated sealed tubes, can nearly colorless samples be obtained.$^{10,26}$ The 2H-CuScO$_2$ reported in Chapter 2 and in literature was a light beige color with low initial levels of oxidation.$^{75}$ If desired, the oxidation can now be controlled through post-annealing methods.
As a wide band gap p-type semiconductor, CuScO$_2$ could have several potential applications in catalysis or photovoltaics. It is likely that in either of these applications an annealing step will be required. For this reason, the influence of annealing under several different conditions on the synthesized CuScO$_2$ absorption and direct band gap was studied. In anticipation of future electrochemical measurements, where good electrical contact between particles is necessary, all samples were annealed at 500 °C under argon atmosphere prior to annealing in air. Figure 9a shows the diffuse reflectance Kubelka-Munk absorption of the as-synthesized CuScO$_2$ and samples annealed at various temperatures. After annealing under argon, the powder turned light gray. Further annealing at 250 °C in air caused a barely detectable change in color. At 350 and 450 °C in air the powders turned dark gray-violet, with a significant increase in absorption around 500 nm. Considering the reported positions of intercalated oxygen into the plane of Cu$^I$ in 2H-CuScO$_2$ (Figure 9b), Cu$^I$ sites are likely oxidized and acquire a near square-planer geometry. Recently, calculation of oxygen interstitial formation enthalpies has shown 4-coordinate copper sites are stable in the bulk.$^{24}$ Thus, this increased absorption can likely be attributed to d–d transitions of Cu$^{II}$. UV-vis spectroscopy of square-planer Cu$^{II}$ complexes also attribute transitions around 500-550 nm to d–d transitions.$^{76}$ The broad increased absorption, particularly extending past 550 nm, could possibly be due to intraband transitions resulting from various oxidized copper or oxygen interstitial states, and again, the reflection of trapped light within the sample resulting in greater absorption. The absorption edges for the direct optical band gaps of the annealed samples are shown in the inset of Figure 9a. At low doping levels (below degeneracy), the optical band gap
is expected to remain the same. Although the accuracy of fitting the absorption edge can decrease as absorption at energies lower than the band transition increases, the approximated gaps of the annealed samples remain within 0.06 eV of the as-synthesized sample.

Figure 9. (a) Kubelka-Munk UV-vis diffuse reflectance spectra of annealed 2H-CuScO$_2$ samples (inset: corresponding absorption edges). (b) 2H-CuScO$_2$ lattice indicating positions of intercalated oxygen. (c) Digital photographs of annealed samples.

*X-ray Photoelectron Spectroscopy of Oxidized 2H-CuScO$_2$*

To explicitly show the increased oxidation of Cu$^I$ to Cu$^{II}$ upon annealing, XPS was performed on the various annealed CuScO$_2$ samples. The Cu 2p spectra are shown in Figure 10. With increased annealing temperature, the Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks broaden. Two distinct new components were fitted at 933.8 eV and 953.6 eV for Cu$^{II}$ 2p$_{3/2}$ and Cu$^{II}$ 2p$_{1/2}$, respectively. In addition, the characteristic Cu$^{II}$ 2p$_{3/2}$ satellite peaks from 940–945 eV appeared and increased in intensity. Satellite peaks occur when an
outgoing core electron excites a valence electron to a higher energy level, reducing the kinetic energy of the core electron. Because these electrons are part of the total Cu 2p emission, the Cu 2p3/2 peak and corresponding satellite peak areas could be used to estimate the ratio of CuI:CuII. Only the 500 °C Ar, 450 °C annealed CuScO2 had sufficient CuII satellite peak intensity to allow for appropriate fitting of each component. The fitted Cu 2p3/2 spectra is shown in Figure 11. Using the combined peak areas, it was estimated that 42.4% of the CuI was oxidized to CuII, corresponding to the formula: CuScO2.21. This estimation assumes every oxygen interstitial is paired around a copper site, leading to a formal oxidation state of 2+. A distribution of oxidation states is likely, considering the possibility of isolated oxygen interstitials, so the assignment of purely CuI and CuII may lead to an underestimation in the oxygen content. For all samples in this work, the Sc 2p, O 1s, and C 1s spectra remained similar.

Figure 10. Cu 2p X-ray photoelectron spectra of annealed 2H-CuScO2.
Figure 11. Cu 2p$_{3/2}$ X-ray photoelectron spectrum of 500 °C Ar, 450 °C air annealed 2H-CuScO$_2$.

$E_{fb}$ Measurements of Oxidized 2H-CuScO$_2$ Films

The increased intercalated oxygen content in CuScO$_2$ by thermal oxidation has been shown to increase conductivity due to increased hole charge carrier density (p).$^{10,35,18}$

\[
\frac{1}{2}O_2 (g) \leftrightarrow O^{2-} + 2h^* \\
p = 2[O^{2-}]
\]

Increases in hole charge carrier density result in lowering of the Fermi level toward the valence band maximum in a semiconductor. Experimentally, the Fermi level can be estimated by determination of the flat-band potential ($E_{fb}$) at a semiconductor-electrolyte interface. If a potential bias is applied to a p-type semiconductor in contact with an electrolyte such that no space charge layer exists in the semiconductor, the conduction
and valence bands are flat at the semiconductor-electrolyte interface and the applied potential is equal to $E_{fb}$. As more negative bias is applied to the semiconductor electrode, its Fermi level moves toward less negative values of energy (in solid state vacuum scale), and the bands bend downward. In the dark, this establishes a barrier to charge transfer and no current flows. Upon illumination with radiation at higher energy than the band gap of the semiconductor, electron-hole pairs are generated and the electrons in the conduction band travel through the interface toward the electrolyte, generating a cathodic photocurrent. Thus, the onset of photocurrent corresponds to the flat-band potential value.

Figure 12 shows the measurement of $E_{fb}$ in a 0.5 M Na$_2$SO$_4$ aqueous solution (pH adjusted to 12.1). The light source was a 435 W Xe lamp and its output was chopped with a mechanical chopper with a frequency of 50 mHz. As the potential bias to the semiconductor was increased toward more negative values, the current under illumination became more negative (i.e. cathodic). This confirmed CuScO$_2$ to be a p-type semiconductor. The photocurrent onset value was obtained by using the Butler method to calculate $E_{fb}$ according to the following equation: $i_{ph}^2 \propto (E - E_{fb})$

where $i_{ph}$ is the photocurrent and $E$ is the applied potential bias. According to this equation, the intercept of the linear region of $i_{ph}^2$ vs $E$ plot with the x-axis will be $E_{fb}$, as shown in Figure 12 ($i_{ph}^2$ plotted on the right-side axes). Indeed, photocurrent increased and the $E_{fb}$ was shifted to more positive potentials vs. NHE: 0.721 V, 0.845 V and 0.938 V for the 250 °C, 350 °C, and 450 °C films, respectively. The PEC behavior and photocurrent response of the film without an air annealing was negligible, likely due to
the CuScO$_2$ being too insulating (i.e. low charge carrier density due to limited oxygen interstitials). A pH of 12.1 was chosen for the aqueous electrolyte to avoid dissolution of the CuScO$_2$, and the lack of clear oxidative and reductive peaks in cyclic voltammograms.

![Figure 12](image.png)

Figure 12. Chopped-light linear sweep voltammograms (left axes) and photocurrent onset potentials (right axes) of annealed CuScO$_2$ films in aqueous 0.5 M Na$_2$SO$_4$ solution (pH = 12.1). (a) 500 °C Ar, 250 °C Air. (b) 500 °C Ar, 350 °C Air. (c) 500 °C Ar, 450 °C

With the large solubility of oxygen interstitials in CuScO$_2$, increases in carrier density resulting in Fermi level shifts are not surprising. Using the Cu$^{II}$ amount determined from XPS, the hole carrier density was estimated to be \( \sim 4.13 \times 10^{21} \text{ cm}^{-3} \).
Comparing this density to a reported undoped CuScO₂ carrier density (~5 x 10¹⁸ cm⁻³) gave an $E_F$ shift of 172 mV. Considering the limitations in both the XPS determination of the Cu²⁺ amount and the photocurrent onset method for flat band determination, a difference between the estimated and measured shifts can be expected. Regardless, the shifts are of the same magnitude.

Finally, XRD patterns of the annealed sample films indicated no clear changes in peak position or shape, as shown in Figure 13. The relative thinness of the plates that formed the hierarchical clusters may help to reduce any strain within the lattice due to intercalated oxygen. Additionally, no changes were observed in the pattern post-photoelectrochemical testing.

![Figure 13. PXRD patterns of annealed CuScO₂ films and after photoelectrochemical (PEC) testing in aqueous 0.5 M Na₂SO₄ solution (pH = 12.1). All films were annealed at 500 °C in argon prior to indicated air annealing.](image)
Unfortunately, the increases in flat-band potential for the CuScO₂ films investigated in this work came at the cost of transparency in the visible range, one of the most attractive properties of the delafossite oxides. For transparent conducting oxide applications, future work on controlling particle size and film preparation, as well as a detailed investigation of oxygen intercalation and the nature of defect states in the hydrothermally prepared delafossite particles, will be necessary.

\textit{p-Type Semiconductor in Dye-Sensitized Solar Cells}

When this work on the synthesis of CuScO₂ was started, the Wu group had established itself in the field of p-type dye sensitized solar cells.\textsuperscript{43,62–72} However, by the time of the publication by Draskovic et.al.\textsuperscript{75}, interest in these dye-sensitized solar cells was waning as new perovskite-based solar cells quickly met performance milestones.\textsuperscript{78} This final section presents preliminary solar cell results utilizing the hydrothermally synthesized CuScO₂ particles as p-type semiconductor films.

In p-type dye sensitized solar cells, visible light absorbing dye molecules are adsorbed on the surface of a p-type semiconductor. Sunlight excites an electron from the highest occupied molecular orbitals (HOMO) of the dye molecules to the lowest unoccupied molecular orbitals (LUMO). Holes left behind in the HOMO are injected into the valance band of the p-type semiconductor and transported to the external circuit. The electron in the LUMO reduces a redox couple in the electrolyte solution (typically I⁻/I₃⁻), which can be oxidized at the counter electrode, giving electrons to the external circuit to combine with the holes. NiO has traditionally been used as the p-type semiconductor, but
absorbs strongly in the visible range and has limited hole mobility, leading to the use of cuprous delafossite oxides.\textsuperscript{60}

To fabricate the CuScO\textsubscript{2} based cells, the oxide films had to first be annealed in air to remove the polymer binder in the paste. They could then be annealed under argon to ensure crystallinity. Based on the results of the previous section, 200 and 350 °C air annealings were chosen to ensure conductivity, but limit parasitic visible light absorption by the film itself. Figure 14 shows the $I$-$V$ curves of the films sensitized with two different dyes using the I$^-$/I$_3^-$ redox couple.

![I-V Curves of annealed CuScO\textsubscript{2} films sensitized by the ruthenium-based O18 and the organic PMI\textsubscript{2}T-TPA dyes using a I$^-$/I$_3^-$ redox electrolyte.](image)

The ruthenium-based O18 dye provided reasonable short-circuit currents ($J_{sc}$), with the 350 °C film more than doubling the current, likely due to increased conductivity. The
organic PMI-2T-TPA dye cell had low currents, but the open-circuit voltage was 204 mV. These values, though poor compared to NiO-based cells, are consistent with other delafossite-based dye-sensitized solar cells.\textsuperscript{60} A high open-circuit voltage could likely not be obtained with the O18 dye due to the HOMO energy of the dye being too negative relative to the conduction band of CuScO\textsubscript{2}, making hole injection energetically unfavorable.\textsuperscript{71,79}

These results provide the first demonstration of CuScO\textsubscript{2} as a p-type semiconductor in dye sensitized solar cells. Considering the extremely large particle size of the hydrothermally synthesized CuScO\textsubscript{2}, it is promising that comparable currents and voltages to other delafossite-based cells were still obtained. Obviously, reduced particle sizes through optimized synthetic methods would help, but in addition, the annealing procedure of the films is also important in obtaining achieving a balance between conductivity and visible light absorption.

3.4 Conclusion

Oxidation of the 2H-CuScO\textsubscript{2} in air at temperatures up to 450 °C gave darkened powders with absorption in the visible range likely due to the increased Cu\textsuperscript{II} content from intercalated oxygen, as shown by XPS. Increasing interstitial oxygen also supported the positive shift seen in the flat band potential as determined by the photocurrent onset of the various oxidized CuScO\textsubscript{2} films. Despite the fact increased hole carrier density led to increased absorption in the visible range, dye-sensitized solar cells utilizing annealed
CuScO$_2$ films as the p-type semiconductor were fabricated. Preliminary results of these optimized cells gave low currents but reached open circuit voltages up to 204 mV.
Chapter 4: Chemical Design of Cuprous Delafossite Oxide Catalysts for Enhanced Oxygen Reduction Activity

4.1 Introduction

As concerns about global climate change and the negative environmental impact of fossil fuel energy sources continue to increase, interest in the development of renewable energy production technologies grows. Efficient electrochemical energy conversion processes are a key component to the successful implementation of renewable energy sources. At their core, each of these processes require efficient and cost-effective catalysts. Of particular interest is the oxygen reduction reaction (ORR) which is utilized in fuel cells and metal-air batteries.\textsuperscript{80,81} Unfortunately, the slow kinetics of the ORR and the necessity for an efficient electrocatalyst has led to limited use of electrochemical energy conversion devices with an air electrode.

Alkaline fuel cells and metal-air batteries are well-established technologies, but the high cost of the current high-efficiency noble-metal ORR catalysts is prohibitive of large-scale commercialization.\textsuperscript{81,82} Transition metal oxide catalysts have shown promise in these systems under alkaline conditions but are still plagued by large overpotentials and a lack of understanding behind the factors governing their catalytic activity. Historically, perovskite oxides have dominated research on ternary metal oxide catalysts,
and recent progress has been made explaining their relatively high observed activities.\textsuperscript{83–85} Regardless, a viable low-overpotential ORR catalyst is still desirable.

As an alternative, the ternary delafossite structured oxides \((A^{I}B^{III}O_{2})\) provide a framework for tuning of chemical and catalytic properties. The unique layered structure allows for the potential enhancement of ORR activities over those of the currently popular perovskite oxide \((A^{II/III}B^{III/IV}O_{3})\) catalysts. Compared to these perovskite oxides, their potential as catalysts is much overlooked. Figure 15 compares the typical structures of perovskite and delafossite oxides.

![Figure 15. Comparison of typical perovskite and delafossite oxide structures.](image)

In this chapter, I provide the novel proposal of a chemical design strategy for cuprous delafossite oxides with enhanced ORR catalytic activity. The delafossite structure possess several key elements that make it desirable for catalytic applications: (1) the presence of low-coordination Cu\textsuperscript{I} sites, which are accessible by \(O_{2}\) molecules; (2) the ability to increase the spacing between the layers by the size of the B\textsuperscript{III} cation, which allows the further tuning of the Cu\textsuperscript{I} accessibility and chemical properties; (3) a wide range of the B-site cations can be used to influence the Cu\textsuperscript{I} site redox, become
catalytically active sites themselves, or potentially for a conductive layer for charge carrier transfer to/from the Cu-site. The most appealing aspect of the structure for potential ORR activity is the linearly-coordinated Cu\textsuperscript{I} sites. Several known proteins and enzymes showing high activity towards O\textsubscript{2} binding or even complete reduction to water contain bi- or tri-nuclear copper active sites with similar Cu\textsuperscript{I}...Cu\textsuperscript{I} distances as those within the Cu\textsuperscript{I} layer of delafossite oxides.\textsuperscript{86}

The studies detailed here on several Cu\textsuperscript{I}-based delafossite oxides can provide insight into the chemical design of not only more delafossite oxide catalysts but potentially more complex oxides with similar tunable active sites.

4.2 Oxygen electrocatalysis

The ORR poses a significant challenge from an electrocatalytic perspective.\textsuperscript{87,88} Most desirable is the reduction of O\textsubscript{2} directly to H\textsubscript{2}O (or OH\textsuperscript{-}, depending on solution pH). Though thermodynamically favorable, the reaction is slow kinetically, requiring the transfer of four electrons and the breaking of the strong molecular O\textsubscript{2} bond (bond dissociation energy = -493.4 kJ mol\textsuperscript{-1}). The competing pathway, occurring at a less positive electrode potential, is a two electron reduction of O\textsubscript{2} to a peroxide (O\textsubscript{2}\textsuperscript{2-}) species. The production of the free, reactive peroxide species can lead to decomposition back to O\textsubscript{2} or unwanted corrosion in many systems. The below equations show the overall reactions for complete and partial reduction of O\textsubscript{2} in acid and alkaline aqueous media:

\textbf{Acidic:} \quad O\textsubscript{2} + 4H\textsuperscript{+} + 4e\textsuperscript{-} \rightleftharpoons 2H_2O \quad E^0 = 1.23 \text{ V (SHE)} \quad (1)
O\textsubscript{2} + 2H\textsuperscript{+} + 2e\textsuperscript{-} \rightleftharpoons H_2O\textsubscript{2} \quad E^0 = 0.695 \text{ V} \quad (2)

\textbf{Alkaline:} \quad O\textsubscript{2} + 2H_2O + 4e\textsuperscript{-} \rightleftharpoons 4OH\textsuperscript{-} \quad E^0 = 0.401 \text{ V} \quad (3)
O\textsubscript{2} + H_2O + 2e\textsuperscript{-} \rightleftharpoons HO_2\textsuperscript{-} + OH\textsuperscript{-} \quad E^0 = -0.065 \text{ V} \quad (4)
Although the chemical equations appear straightforward, the exact mechanisms by which the multiple electron transfers occur are subject to debate. Further complicating matters, the mechanism can be influenced by the electrode material, applied potential, and solution. The simplest of the complete reduction mechanisms is the dissociative (shown in alkaline solution):\(^{89,88}\)

\[
\begin{align*}
\frac{1}{2}O_2 + M & \rightarrow M-O \\
M-O + H_2O + e^- & \rightarrow M-OH + OH^- \\
M-OH + e^- & \rightarrow M + OH^- 
\end{align*}
\]

Here, \(M\) denotes a surface site. The reaction can also take place without the direct dissociation of \(O_2\) via a peroxy intermediate, in what is known as the associative mechanism (shown in alkaline solution):\(^{88,89}\)

\[
\begin{align*}
O_2 + M & \rightarrow M-O_2 \\
M-O_2 + H_2O + e^- & \rightarrow M-O_2H + OH^- \\
M-O_2H + e^- & \rightarrow M-O + OH^- \\
M-O + H_2O + e^- & \rightarrow M-OH + OH^- \\
M-OH + e^- & \rightarrow M + OH^- 
\end{align*}
\]

The formation of the surface peroxy intermediate in the associative mechanism allows for the potential desorption and further reaction of the peroxy species, resulting in only the two electron reduction of \(O_2\).
The slow kinetics of the ORR must be increased in order to allow for significant current densities to be obtained from the electro-reduction of oxygen. The kinetic barrier can be lowered through the use of electrocatalysts and also by reducing the electrode potential. The difference between the electrode potential \( (E) \) and the equilibrium potential of the electrode reaction \( (E_{eq} = 1.23V) \) is known as overpotential, \( \eta \). By increasing reaction kinetics, electrocatalysts can increase the currents obtained at all overpotentials, thereby allowing for the lowering of overpotential while still maintaining necessary currents.

Currently, platinum and platinum alloys are the most widely used electrocatalysts for the ORR in various applications. The predominant “activity descriptor” for these platinum-based catalysts is based on the d-band model, relating surface metal d-orbitals and chemisorbed molecular orbitals.\textsuperscript{90–92} According to this model, as the center of the metal d-band shifts up, an antibonding state appears above the Fermi level. Antibonding states above the Fermi level are empty, so bonds with adsorbed species become increasingly stronger as the number of these states increases. Thus, strong bonding occurs if the antibonding states are shifted up though the Fermi level (becoming empty), and weak bonding occurs if antibonding states are shifted down below the Fermi level (becoming filled). With the application of the Sabatier principle, this led to creation of so-called “volcano” relationships for metals and platinum alloys.

Various metal oxides have shown catalytic activities comparable to those of platinum based catalysts, particularly when used in alkaline aqueous electrolytes. The perovskites LaCoO\(_3\) and LaNiO\(_3\) were recognized for high ORR activity in the early
More recently, research on perovskite oxides has led to the determination of several factors governing oxide ORR activity. The perovskite ABO$_3$ structure allows for partial substitution at both the A and B-sites for control of catalytic properties. Varying combinations of transition metals at the B-site of lanthanum based perovskites allows for the tuning of $e_g$ orbital occupation and metal-oxygen covalency of surface MO$_6$ octahedra. Suntivich et al. proposed that a localized surface $e_g$ occupation of ~1 leads to the highest activity by destabilizing the M-OH$^-$ bond and promoting O$_2^2$-/OH$^-$ exchange.

Currently, efforts are focused on tuning Pt-based catalysts to limit the amount of platinum necessary and lower costs. However, although these catalysts may currently be the best available and the potential for cost-reduction exists, they still require significant overpotentials to achieve useful current densities. Perovskite oxides are a viable alternative and have received significant attention, but reported performances are still behind those of platinum. The need for a non-precious metal based ORR catalyst with the possibility of equal or better activities than platinum still exists, and the following details why the delafossite family of oxides may contain an appealing candidate.

### 4.3 O-Cu$^{1-}$-O as Catalytic Centers

The linearly coordinated Cu$^1$ sites are perhaps the most interesting aspects of delafossite compounds. Unlike cuprous oxide (Cu$_2$O), which also consists of linearly coordinated Cu$^1$ atoms, delafossite oxides have layers of parallel O-Cu$^{1-}$-O units. This forms a two-dimensional network of copper atoms. The spacing and possible interaction between copper atoms in this network can be tuned by altering the size of the B-site cation. A wide range of copper-copper distances (equivalent to the $a$ lattice
parameter) are possible, as shown in Figure 16a. The distances range from 2.85 Å for CuCoO$_2$ to 3.83 Å for CuLaO$_2$. This space between copper atoms within the O-Cu$^1$-O layer has been shown to allow for reversible oxygen intercalation without decomposition of the delafossite phase. In particular, delafossite oxides with B-site ionic radii equal to or larger than Sc$^{III}$ can accommodate excess oxygen up to $x = 0.66$ in the general formula CuB$^{III}$O$_{2+x}$. Nearly all studies of oxygen uptake were performed at elevated temperatures in air or oxygen environments, however, room temperature chemical oxidation by aqueous hypohalite solutions was demonstrated for CuYO$_2$ and CuLaO$_2$, both delafossite oxides with large (> 3.5 Å) Cu···Cu distances. Refinement of neutron diffraction data has confirmed that oxygen intercalates into the plane of copper atoms, giving rise to a square planar geometry suitable for Cu$^{II}$, as in CuO (Figure 16b). The thermal and chemical oxidation of delafossite oxides demonstrates the potential of the linearly coordinated Cu$^1$ sites to interact with O$_2$ under relatively mild conditions without phase decomposition.
Figure 16. (a) Variation of the a lattice constant (Cu···Cu distance) with B-site ionic radius. (b) Delafossite structure indicating position of intercalated oxygen; copper (blue spheres), oxygen (red spheres), B-site (green octahedra).

Biology also provides support for potential ORR catalysis at delafossite CuI sites. Several proteins and enzymes have mono-, bi-, or tri-nuclear copper sites that have been shown to bind to O₂.\textsuperscript{86,105,106} Dopamine β monoxygenase and peptidylglycine α-hydroxylating monoxygenase contain isolated single copper active sites.\textsuperscript{107} Oxygen can σ-bond to the copper site in an end-on fashion through one π* orbital to undergo one electron reduction, forming a bound superoxo (Cu\textsuperscript{II}-O₂\textsuperscript{−}), which can then abstract hydrogen atom from a biological substrate. The hemocyanin protein and tyrosinase enzyme have binuclear CuI sites that bind to O₂ forming a side-on peroxo bridged binuclear Cu\textsuperscript{II} structure.\textsuperscript{105} The distance between the two bridged copper atoms is approximated at 3.6 Å. Important to this structure is that the unoccupied σ* orbital of the peroxide is oriented to interact with occupied copper d-orbitals, as shown in Figure 17.\textsuperscript{108} This backbonding interaction shifts electron density into the σ* orbitals, significantly weakening to O-O bond. Multicopper oxidase enzymes contain a trinuclear copper site
with a neighboring fourth copper, which can catalyze the four electron reduction of O\textsubscript{2} to water. Binding of O\textsubscript{2} occurs within the trinuclear center through various bridged intermediates.\textsuperscript{105} The distances between these three copper atoms when bridged by oxygen species are also around 3.5 Å. The presence of four Cu\textsuperscript{I} sites allows for the four electron transfer to occur in to two concerted steps: two electrons into the \( \pi^* \) orbitals, followed by two electrons into the \( \sigma^* \) orbital. With the transfer of four electrons and four protons from the substrate, the four copper sites are reduced and the bound oxygen is released as water.

![Molecular orbital diagrams of end-on and side-on bridged binuclear copper sites. Side-on bridging allows electron density in the \( \sigma^* \) orbital of O\textsubscript{2}^2-.](image)

**Figure 17.** Molecular orbital diagrams of end-on and side-on bridged binuclear copper sites. Side-on bridging allows electron density in the \( \sigma^* \) orbital of O\textsubscript{2}^2-.

The (\( hk0 \)) surfaces of the delafossite structure have exposed alternating O-Cu\textsuperscript{I}-O and B\textsuperscript{III}O\textsubscript{6} layers. To isolate the Cu\textsuperscript{I} as a potential catalytic site, redox stable closed-shell trivalent B-site cations will be used. These include the group 3 and group 13 elements: Al\textsuperscript{III}, Ga\textsuperscript{III}, Sc\textsuperscript{III}, Y\textsuperscript{III}, and La\textsuperscript{III}. Coincidentally, these elements also provide a wide range of Cu\textsuperscript{I}--Cu\textsuperscript{I} distances: 2.86 Å, 2.97 Å, 3.22 Å, 3.52 Å, and 3.83 Å, respectively.\textsuperscript{25} The
latter Cu\textsuperscript{I}···Cu\textsuperscript{I} distances are interestingly within the range of those within copper-based proteins and enzymes. Knowing that bridging of two or more copper atoms by O\textsubscript{2} species is favored in biological active sites, several possible binding modes for O\textsubscript{2} at the Cu\textsuperscript{I} sites in delafossite oxides can be proposed, as shown in Figure 18\textsuperscript{109,110,108,86}.

Concerning the delafossite oxides with shorter Cu\textsuperscript{I}···Cu\textsuperscript{I} distances (CuAlO\textsubscript{2}, CuGaO\textsubscript{2}, and likely CuScO\textsubscript{2}), O\textsubscript{2} should only be able to bind at one copper site due to poor orbital overlap for bridging or steric constraints. This single site binding could allow for the associative mechanism of oxygen reduction as shown previously in Equations 8-12. However, when the Cu\textsuperscript{I}···Cu\textsuperscript{I} distances are increased, as in CuYO\textsubscript{2}, and CuLaO\textsubscript{2}, a bridged binuclear binding mechanism becomes plausible. The potential for this bridging mechanism is significant in that it weakens the O-O bond in the early stages of the reaction, possibly leading to oxygen dissociation following Equations 5-7. The dissociative mechanism should lead to increased reaction kinetics and a low likelihood for peroxide species formation.

Even though the distances between copper atoms in the delafossite oxides can be similar to those within active copper-centered proteins and enzymes, the differences in
geometry and chemical environment of the copper species cannot be ignored. In biological active sites, Cu\(^I\) is typically 2- or 3-coordinate.\(^{86,105}\) When oxidized, the now \(d^9\) Cu\(^{II}\) sites are stable 4-coordinate square planar or 5-coordinate square pyramidal.

Although bulk Cu\(^I\) is linearly coordinated in the delafossite structure, the localized nature of surface states, along with the thermodynamic instability of Cu\(^I\) (particularly in CuYO\(_2\) and CuLaO\(_2\)) should drive the increased coordination and oxidation of copper at the surface during oxygen binding. Depending on the binding mode of O\(_2\), further ligands could be provided by hydroxide (relatively abundant in alkaline electrolytes) or by a neighboring copper-bridged oxygen species. Another key difference between biological active sites and the delafossite copper sites is the rigidity of the structure. Unlike in the rigid crystalline lattice of oxides, the available degrees of freedom provided by the surrounding organic ligands in proteins and enzymes allow for the Cu···Cu distances vary slightly upon binding and release of O\(_2\). However, as previously discussed, the ability to tune the distances between copper atoms in delafossite oxides through choice of B-site is hoped to allow for similar binding mechanisms to occur.

4.4 B\(^{III}\)O\(_6\) Octahedra as Catalytic Centers

The (00\(_l\)) surfaces of delafossite crystals have been calculated and determined to be terminated by the oxygen of the B-site octahedra in air at room temperature.\(^{24}\) Therefore, depending on the crystallite size and morphology, it is possible the majority of a delafossite particle surface could be the exposed octahedra. Considering the potential activity at the B-site octahedra, there are only several transition metals available for incorporation into the delafossite structure. As mentioned before, the group 3 and group
13 trivalent metals are known to be relatively inert with respective $d^0$ and $d^{10}$ ($p^6$ for Al$^{III}$) closed-shell configurations. The likely candidates (considering the long-term goal of becoming a cost-effective alternative catalyst) are therefore CuCrO$_2$, CuMnO$_2$, CuFeO$_2$, and CuCoO$_2$. In each compound the B-site is trivalent with $d^3$, $d^4$ (HS), $d^5$ (HS), and $d^6$ (LS) configurations, respectively.$^{111-113}$

The electronic configurations of these delafossite B-sites are similar to those of the lanthanum-based perovskites with the same transition metal B-site.$^{83}$ Even though the proposed activity descriptors for perovskites may not directly apply to all ternary oxide catalysts containing transition metal octahedra (i.e. delafossite and spinel oxides), oxides with significant reported catalytic activities typically contain Mn$^{III}$, Fe$^{III}$, or Co$^{III}$ octahedra as the claimed catalytic site.$^{114-118}$ Regardless of octahedra orientation, the occupation of $e_g$ orbitals appears to be necessary for oxygen reduction activity. Considering these are the only $d$ orbitals that can $\sigma$-bond with oxygen species, the necessity for their partial filling can be rationalized. Considering this, CuCrO$_2$ will likely show the smallest ORR activity. Determination of the catalytic activities for this series of delafossite oxides should also contribute to back to the developing knowledge and description of transition metal octahedra in perovskite and spinel oxides, hopefully allowing for better design of oxide catalysts in the future.

As discussed in the previous section, the copper sites of the CuCrO$_2$, CuMnO$_2$, CuFeO$_2$, and CuCoO$_2$ delafossite oxides could still potentially participate in oxygen reduction. However, the Cu$^{I}$⋯Cu$^{I}$ distances in each of these compounds are fairly similar and relatively short (< 3.0 Å), which should limit their influence. Regardless, a better
understand of the copper site activities will be developed before introducing these potentially active B-sites.

4.5 Plan of Work

The goal of this chapter is to provide convincing support for the catalytic activity of delafossite oxides towards the oxygen reduction reaction. Using previous work on transition metal catalysts (both inorganic and biological) as justification, potential mechanisms for activity were detailed. Concerning the broad scope of this proposed application, detailed investigations to support these proposed mechanisms will be the focus of future work. As discussed in the following chapters, relatively simple high temperature syntheses, characterization, and initial measurements of activity toward oxygen electrocatalysis were first attempted.
Chapter 5: Cuprous Delafossite Oxides for Alkaline Oxygen Electro catalysis

5.1 Introduction

Efficient electrochemical energy conversion processes are a key component to the successful implementation of renewable energy sources. At their core, each of these processes require efficient and cost-effective catalysts. Of particular interest is the oxygen reduction reaction (ORR), which is utilized in fuel cells\textsuperscript{80,119} and metal-air batteries.\textsuperscript{81,120,121} Unfortunately, the slow kinetics of the ORR and the cost of high-efficiency noble-metal catalysts has led to limited use of electrochemical energy conversion devices with an air electrode. Transition metal oxide catalysts have shown promise in these systems under alkaline conditions, and historically, perovskite oxides have dominated research on metal oxide catalysts.\textsuperscript{83–85,122,123} Recent progress has been made explaining their relatively high observed activities towards oxygen reduction.\textsuperscript{122} Regardless, finding a viable low-overpotential ORR catalyst is still the focus of much research.\textsuperscript{123}

Looking to nature for inspiration, several proteins and enzymes have mono-, bi-, or tri-nuclear copper sites that have been shown to bind to O\textsubscript{2}.\textsuperscript{86} For example, binuclear Cu\textsuperscript{I}-site proteins and enzymes bind to O\textsubscript{2} forming a side-on peroxo bridged structure with an interatomic copper distance near 3.6 Å.\textsuperscript{86,105} Important to this structure is that the unoccupied peroxide $\sigma^*$ orbital interacts with occupied copper d-orbitals, significantly
weakening to O-O bond. Multicopper oxidase enzymes containing a trinuclear copper site with a neighboring fourth copper can directly catalyze the four electron reduction of O2 to water.\textsuperscript{86,105} Recently, the catalytic activity of Cu\textsubscript{2}O oxide nanocrystals towards alkaline ORR was reported, demonstrating the potential for a copper active site in oxides.\textsuperscript{124,125}

Copper delafossite structured oxides provide an interesting framework for tuning of chemical and catalytic properties. Similar to other widely studied ternary oxides, the delafossite oxides can support a range of chemical compositions, however, the structure is unique with alternating layers of linearly coordinated O–Cu\textsuperscript{I}–O and B\textsuperscript{III}O\textsubscript{6} edge-shared octahedral (Figure 1b).\textsuperscript{9} The interatomic Cu-site distance scales with B-site ionic radii, allowing for a range of 2.85 – 3.83 Å. Interestingly, the multicopper active sites of proteins and enzymes have interatomic copper distances around 3.5– 3.6 Å, well within the range of distances found in delafossite oxides. The delafossite structure has the potential to allow tunability of the copper site through interatomic distances or electronic interaction with the B-site. Copper A-site delafossite oxides are also of particular interest due to their various possible syntheses,\textsuperscript{24,34,126} the multiple oxidation states of copper,\textsuperscript{10,21,127} and the relative abundance of copper compared to other transition metal species. The first reported application of copper delafossite oxides toward oxygen electrocatalysis focused on varying the B-site to study oxygen evolution reaction (OER) catalysis.\textsuperscript{128,129} Tuning orbital occupancy at the B-site led to discovery of a relatively high catalytic OER activity. The numerous potential B-site compositions in delafossite oxides are appealing for catalytic applications, but the activity of the copper A-site has not been investigated.
The series of group 3 B-site delafossite oxides Cu(Sc,Y,La)O$_2$ was chosen first to investigate the catalytic activity of the copper site toward ORR. Trivalent scandium, yttrium and lanthanum are $d^0$ and not expected to be redox active themselves. In addition, lanthanum based perovskite oxides have been used extensively to study various transition metal active sites in ORR electrocatalysis. The interatomic copper distances range from 3.22 to 3.83 Å, which includes those distances found in biological active sites. This could potentially allow for terminal or bridged binding of oxygen species. These three oxides are also interesting members of the delafossite family in that the large interatomic distances between copper atoms allow for oxygen intercalation reaching CuBO$_2$.66, while maintaining the layered structure. Interesting magnetic properties and increased conductivity arise from this high oxidation. Moreover, electronic structure calculations predict insertion of oxygen interstitials forms a partially-filled impurity band of Cu 3$d_{xy}$- $d_{x^2-y^2}$ and O 2$p_x$,$p_y$ character around the Fermi level, rather than within the valance O 2$p$ bands. The nature of this band suggests the possible binding/exchange interaction between surface copper and molecular oxygen species for delafossite oxides.

In this chapter, CuScO$_2$, CuYO$_2$, CuLaO$_2$ and CuLaO$_2+x$ were synthesized and their potential as ORR electrocatalysts was evaluated through rotating disk electrode measurements. Clear enhancement of activity was observed over the carbon black support, with CuLaO$_2$ exhibiting the highest preference toward the complete reduction process. Finally, CuRhO$_2$, with a potential catalytically active B-site was tested for ORR and OER. The potential for a new family of oxide catalysts for oxygen electrocatalysis was demonstrated.
5.2 Experimental

Materials. Copper (I) oxide (97%, Sigma-Aldrich), copper (II) oxide (98%, Sigma-Aldrich), scandium (III) oxide (99.9% Sigma-Aldrich), yttrium (III) oxide (99.99% Sigma-Aldrich), lanthanum (III) oxide (99.99% Alfa Aesar), Super P Li Carbon (TIMCAL), Nafion (5% wt. solution, Sigma-Aldrich), sodium hydroxide (certified ACS, Fisher Scientific), potassium hydroxide (90%, Sigma Aldrich), de-ionized water ($\rho = 18$ MΩ·cm, Barnstead E-Pure), argon (99.998%, Praxair, Inc.), and oxygen (99.993%, Praxair, Inc.). Rhodium (III) oxide was prepared by heating RhCl$_3$ hydrate in air at 800 °C. Lanthanum (III) oxide was dried at 1000 °C immediately prior to use. All other materials were used without further purification.

Solid State Synthesis. Following previous literature reports, typical solid state syntheses of CuScO$_2$, CuYO$_2$, and CuLaO$_2$, were performed. CuScO$_2$ was synthesized by the decomposition of Cu$_2$Sc$_2$O$_5$ under argon at 1050 °C for 36 hours.$^{22,26}$ Cu$_2$Sc$_2$O$_5$ was first prepared by the heating of CuO and Sc$_2$O$_3$ at 1000 °C in air for 24 hours. CuYO$_2$ was synthesized by similar methods with the decomposition of Cu$_2$Y$_2$O$_5$ under argon at 1050 °C for 36 hours, the Cu$_2$Y$_2$O$_5$ being prepared by the reaction of CuO and Y$_2$O$_3$ at 1000 °C in air for 24 hours.$^{22}$ CuLaO$_2$ was synthesized by heating of Cu$_2$O and La$_2$O$_3$ in an evacuated silica tube at 1050 °C for 72 hours.$^{22}$ CuLaO$_{2.66}$ is difficult to prepare without some stacking faults or the presence of additional less-oxidized phases. Regardless, the best reported synthesis involves heating CuLaO$_2$ at 280 °C for 4 days under flowing
CuRhO$_2$ was synthesized by heating of Cu$_2$O and Rh$_2$O$_3$ in air at 1050 °C for 12 hours.$^{128}$

Characterization Methods. Products were characterized by powder X-ray diffraction (PXRD) with a Rigaku Corp. Geigerflex using Cu Kα$_1$ radiation. Scanning electron microscopy (SEM) images were obtained with an FEI/Philips Sirion Field Emission SEM. X-ray photoelectron spectroscopy (XPS) characterization was performed with a Kratos Axis Ultra XPS spectrometer using monochromatic Al Kα radiation at an operating voltage of 12 kV and a current of 10 mA. The sample powder was pressed onto carbon tape on the sample holder, and an electron flood gun was used to avoid surface charging problems. Spectra fitting was performed with the CasaXPS software according to previously reported parameters, using combined Gaussian–Lorentzian profiles with a Shirley-type background.$^{37}$

Rotating-Disk Electrode Electrochemistry. The electrocatalytic properties of the oxides were measured using a previously developed thin-film rotating disk electrode method.$^{133}$ Carbon black (Super P Li) and Na$^+$-exchanged Nafion binder were used as a conductive support and binder to facilitate dissolved oxygen transport, respectively. The catalyst mixtures were prepared in a 5 mg$_{\text{catalyst}}$ mL$^{-1}$: 1 mg$_{\text{carbon}}$ mL$^{-1}$: 1 mg$_{\text{nafion}}$ mL$^{-1}$ ratio in ethanol and 8 μL of the mixture were dropcast on a glassy carbon working electrode (Pine Instrument). All electrochemical tests were performed in three-electrode glass cell (Pine), using a rotator (Pine), and the potential was controlled using a Gamry Reference 600 potentiostat. A 0.1 M KOH electrolyte was saturated with argon or oxygen prior to
measurements. Oxygen evolution reaction measurements were performed in oxygen saturated 0.1 M KOH with a 1600 rpm rotation. All scan rates were 10 mV s\(^{-1}\).

5.3 Results/Discussion

Influence of Cu-Cu Distances

Powder X-ray diffraction (PXRD) of the Cu(Sc,Y,La)O\(_2\) compounds is shown in Figure 19. CuScO\(_2\) contains a mixture of both the \(R-3m\) \((a = 3.222(1) \text{ Å}, c = 17.106 \text{ Å})\) and \(P6_3/mmc\) \((a = 3.221(1) \text{ Å}, c = 11.404 \text{ Å})\) polytypes. CuYO\(_2\) also contains a mixture of both the \(R-3m\) \((a = 3.522(2) \text{ Å}, c = 17.143 \text{ Å})\) and \(P6_3/mmc\) \((a = 3.522(3) \text{ Å}, c = 11.417 \text{ Å})\) polytypes. Asterisks (*) mark the peaks due to the hexagonal polytypes. The pattern for CuLaO\(_2\) is consistent with literature for the rhombohedral \(R-3m\) polytype \((a = 3.822(3) \text{ Å}, c = 17.073(1) \text{ Å})\). Despite the mixed polytypes present in CuScO\(_2\) and CuYO\(_2\), the \(a\) lattice parameters are the same, within error, indicating that the interatomic copper distances can be estimated as 3.22, 3.52, and 3.83 Å for CuScO\(_2\), CuYO\(_2\), and CuLaO\(_2\), respectively. Concerning particle size, it can be expected with high temperature solid state syntheses that large, often agglomerated particles can form. Indeed, scanning electron microscopy (SEM) of the three compounds revealed particle sizes on the order of 1 μm, with some larger (>2 μm) agglomerates as shown in Figure 20.
Figure 19. PXRD pattern of CuScO$_2$, CuYO$_2$, and CuLaO$_2$. Asterisks (*) indicate peaks solely from the 2H polytypes.

The electrocatalytic properties of the oxides were measured using a previously developed thin-film rotating disk electrode method.$^{133}$ Carbon black and Na$^+$-exchanged Nafion binder were used as a conductive support and binder to facilitate dissolved oxygen transport, respectively. The catalyst mixtures were dropcast on a glassy carbon
working electrode. All electrochemical tests were performed in argon or oxygen-saturated 0.1 M KOH. The cyclic voltammograms under argon indicate a pair of redox peaks in the CuScO$_2$, CuYO$_2$, and CuLaO$_2$ samples, likely due to the Cu$^{1}$/Cu$^{II}$ redox couple (Figure 21). Reasonably, the peak positions match well with those reported for Cu$_2$O under similar conditions.$^{125}$ The presence of these peaks in all three oxides confirms that the surface Cu$^{1}$/Cu$^{II}$ redox couple is active in this potential range.

Figure 21. Cyclic voltammograms of CuScO$_2$, CuYO$_2$, and CuLaO$_2$ thin-film electrodes in argon-saturated 0.1 M KOH.

Rotating disk electrode (RDE) measurements were performed to determine the catalytic activity of the carbon-supported oxides. Figure 22a shows the typical ORR current densities of CuLaO$_2$ at a rotation rates of 100, 400, 900, and 1600 rpm. RDE
measurements allowed for the application of the Koutecky-Levich equation to the catalyst current densities in the diffusion-limited region:

$$\frac{1}{i_{\text{lim}}} = \frac{1}{i_k} + \frac{1}{(0.62nFD^{2/3} \omega^{1/2} \nu^{-1/6} C)}$$

Where, \( n \) is the number of electrons transferred, \( F \) is the Faraday constant, \( D \) is the diffusion coefficient of \( \text{O}_2 \) \((1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})\), \( \omega \) is the electrode rotation rate, \( \nu \) is the kinematic viscosity of water \((0.01 \text{ cm}^2 \text{ s}^{-1})\), and \( C \) is the concentration of \( \text{O}_2 \) in 0.1 M KOH aqueous solution \((1.2 \times 10^{-6} \text{ mol cm}^{-3})\). A plot of \( i_{\text{RDE}}^{-1} \) in the diffusion limited region over \( \omega^{-1/2} \) allows for calculation of the electron transfer number from the slope and the kinetic current \( (i_k) \) from the y-intercept (Figure 22b). The diffusion-limited region of RDE currents is typically constant due to the current being limited solely by the diffusion of the species to be catalyzed to the electrode at a specific rotation rate. The RDE linear sweep voltammograms in this work display a small “peak” in the diffusion-limited region. Previous literature demonstrated the effect of film thickness on this feature for carbon-supported platinum catalyst, finding it more prominent in thicker films. The authors suggested this was due to the ignition reduction of \( \text{O}_2 \) adsorbed within the electrode film. Regardless, the Koutecky-Levich plots were shown to remain similar despite the film thickness. Attempts to prepare thinner films in this work led to non-uniform films.
Figure 22. (a) Rotating-disk linear sweep voltammetry of CuLaO$_2$ in oxygen-saturated 0.1 M KOH. (b) Koutecky-Levich plots of CuScO$_2$, CuYO$_2$, and CuLaO$_2$ at 0.460 V vs. RHE.

A comparison of the linear sweep voltammograms of CuScO$_2$, CuYO$_2$, and CuLaO$_2$ at 1600 rpm shows nearly identical onset potentials and diffusion limited currents. This is not surprising considering the catalytic active site of the three oxides is expected to be the linearly coordinated copper A-sites. Cyclic voltammetry indicating similar peaks also supports that, despite the structural and chemical changes, the active sites remain the same. The slight differences in diffusion limited current between the oxides could be due to slight differences in the active surface area of the particles. The activity of the carbon black and Nafion support without oxide is also shown in Figure 23. The carbon-supported oxides show better ORR activity than the carbon black in terms of onset potential and half-wave potential. Compared to the previously reported carbon-supported Cu$_2$O, these delafossite oxides showed very similar activities relative to carbon
black. Encouragingly, those Cu$_2$O nanoparticle catalysts had well-defined copper surfaces whereas this initial study used larger solid state synthesized delafossite oxide particles, whose limitations are further discussed later.

![Figure 23. Linear sweep voltammograms of CuScO$_2$, CuYO$_2$, CuLaO$_2$, and the carbon black support in oxygen-saturated 0.1 M KOH (Rotation rate: 1600 rpm).](image)

The electron transfer numbers at various potentials in the diffusion limited region are shown in Figure 24a. The reduction of oxygen can either occur by the two electron pathway to a peroxide intermediate or the complete four electron reduction to hydroxide in alkaline solution. The complete reduction is preferred over formation of the reactive/corrosive peroxide species. CuScO$_2$ and CuYO$_2$ have electron transfer numbers in the range of $n = 2.1$-$2.2$. Both oxides have similar calculated $n$ values at each potential.
The values are only a slight improvement over the carbon black support \((n = 2)\), despite the enhanced onset potentials. Encouragingly, CuLaO\(_2\) has electron transfer numbers in the range of \(n = 2.3-2.9\). In addition, the fact that the activity of the carbon support is non-negligible in this potential region suggests the values solely due to the oxide active sites are likely higher. Figure 24b is the ORR Tafel plot for the catalysts using the kinetic currents derived from the Koutecky-Levich equation. Again, clear enhancement of the currents for the oxides can be seen over the carbon black support. The Tafel slopes are \(-59\), \(-55\), \(-56\), and \(-53\) mV dec\(^{-1}\) for the CuScO\(_2\), CuYO\(_2\), CuLaO\(_2\), and carbon black, respectively. These values are close to the \(-59\) mV dec\(^{-1}\) typically attributed to a rate determining step involving migration of adsorbed oxygen intermediates, and observed for perovskite oxides under similar conditions.\(^{133}\) Although the Koutecky-Levich analysis is a useful and widely used technique for studying catalytic activity, some caution must be taken with the interpretation of the results. The electron transfer number and Tafel slope are helpful in further distinguishing the enhanced activity from addition of the oxides, but the carbon support still provides a non-negligible contribution to the total ORR activity. Furthermore, detailed rotating ring-disk electrode measurements are preferred for unambiguous determination of the ORR product.
Figure 24. (a) Electron transfer number \((n)\) and (b) Tafel plots calculated from the Koutecky-Levich equation for RDE data of CuScO\(_2\), CuYO\(_2\), CuLaO\(_2\), and the carbon black support. All potentials were \(iR\)-corrected. Error bars for electron transfer number represent at least three trials.

Finally, even though the carbon-support can influence observed activities and not allow for a determination of the intrinsic oxide activity, it is widely accepted in catalytic studies. Typically, low current densities and poor fits to the Koutecky-Levich equation are obtained when the carbon support is not used with low conductivity oxides.\(^{125}\) Figure 25 shows the activity of a CuLaO\(_2\) electrode prepared as before, but without the carbon black. The activity was clearly limited, with an onset potential and diffusion limited current much lower than that of carbon itself.
Influence of CuLaO$_{2+x}$ Oxidation

Although CuScO$_2$, CuYO$_2$, and CuLaO$_2$ had similar onset potentials, CuLaO$_2$ had noticeably higher preference toward the complete reduction of oxygen. Despite the fact the interatomic copper distance of 3.83 Å in CuLaO$_2$ is slightly larger than those found in biological active sites, the spacing could allow for bridged binding of oxygen species. Bridged binding would increase the likelihood of breaking the O-O bond and continuing with the complete reduction by the dissociative mechanism. CuLaO$_2$ is also an interesting member of the delafossite family in that these large interatomic distances between copper atoms allow for oxygen intercalation reaching CuLaO$_{2.66}$, while maintaining the layered structure. In order to study the influence of this increase oxidation, CuLaO$_{2+x}$ was
synthesized and the potential as an ORR electrocatalyst was evaluated through rotating disk electrode measurements.

The fully oxidized form, CuLaO$_{2.66}$, is difficult to prepare without some stacking faults or the presence of additional less oxidized phases. PXRD patterns are shown in Figure 26, comparing the as-synthesized and oxidized phases. The oxidized CuLaO$_2$ sample pattern matches well with the reported $P$-31$c$ CuLaO$_{2.66}$ ($a = 6.691(2)$ Å, $c = 10.406$ Å). Several low intensity peaks, most notable around 28°, often appear in these heavily oxidized compounds due to ill-ordered or lower oxidation phases. No peaks match decomposition products such as CuO or the tetragonal CuLa$_2$O$_4$. Considering the scope of this work, the oxidized compound tested will be referred to as CuLaO$_{2+x}$.

![Indexed PXRD patterns and structures showing the differences between the R-3$m$ CuLaO$_2$ and P-31$c$ CuLaO$_{2+x}$ compounds.](image)

Figure 26. Indexed PXRD patterns and structures showing the differences between the $R$-$3m$ CuLaO$_2$ and $P$-31$c$ CuLaO$_{2+x}$ compounds.
Cyclic voltammetry in argon-saturated 0.1 M KOH indicated a similar pair of redox peaks in CuLaO$_{2+x}$ samples as the un-oxidized delafossite samples, likely due to the Cu$^{I}$/Cu$^{II}$ redox couple (Figure 27a). The presence of these peaks in both oxides confirms that despite the varying amounts of oxidation, the surface Cu$^{I}$/Cu$^{II}$ redox couple remains active in this potential range. Figure 27b shows the typical capacitance-corrected ORR current densities at a rotation rate of 1600 rpm. CuLaO$_2$ and CuLaO$_{2+x}$ have nearly identical onset potentials and diffusion limited currents. This is somewhat surprising considering the greater bulk conductivity of the oxidized phase. However, considering the low conductivity of the oxides relative to the carbon black support, changes in bulk oxide conductivity are likely negligible toward the observed catalytic current. The cyclic voltammetry and similar catalytic onset potentials again suggest that despite the structural and chemical changes, the active site remains the same. The slight decrease in diffusion limited current for CuLaO$_{2-x}$ could be due to the structural disorder or agglomeration induced by the low temperature annealing.
Figure 27. (a) Cyclic voltammograms of CuLaO$_2$ and CuLaO$_{2+x}$ thin-film electrodes in argon-saturated 0.1 M KOH. (b) Linear sweep voltammograms in oxygen-saturated 0.1 M KOH (Rotation rate: 1600 rpm).

The Koutecky-Levich equation was applied to the catalyst RDE current densities at 100, 400, 900, and 1600 rpm. CuLaO$_2$ and CuLaO$_{2+x}$ have electron transfer numbers in the range of $n = 2.2$-2.9, as shown in Figure 28a. Both oxides have similar calculated $n$ values at each potential. Again, the fact that the activity of the carbon support is non-negligible in this potential region suggests the values solely due to the oxide active sites are likely higher. Figure 28b is the ORR Tafel plot for the catalysts using the kinetic currents derived from the Koutecky-Levich equation. The Tafel slopes are -56, and -58 mV dec$^{-1}$ for CuLaO$_2$ and CuLaO$_{2+x}$, respectively. These values are again close to the -59 mV dec$^{-1}$ typically attributed to a rate determining step involving migration of adsorbed oxygen intermediates.
The similarities in activity between the two samples is somewhat surprising considering the significant increase in oxygen content and structural changes in the CuLaO$_{2+x}$. To provide a better chemical characterization of the catalyst surfaces directly, the carbon-supported oxide films were transferred from the glassy carbon to carbon tape for X-ray photoelectron spectroscopy (XPS). Figure 29 shows the Cu 2p region for CuLaO$_2$ and CuLaO$_{2+x}$ catalyst films before and after electrochemical testing.
Both samples initially have significant Cu$^{\text{II}}$ amounts from their syntheses and the compound’s ease of oxidation. The surface abundance of Cu$^{\text{I}}$/Cu$^{\text{II}}$ in CuLaO$_{2+x}$ remains similar to CuLaO$_2$ despite the change in bulk oxidation. Little change is also seen in the spectra after testing, with only a slight reduction in the relative Cu$^{\text{II}}$ 2p intensity for the CuLaO$_{2+x}$. Similar surface oxidation could explain the similar ORR activities despite the structural and chemical changes in the bulk. In other words, the copper active site environment appears to remain relatively unchanged after further oxidation.

*Potential Active B-Site of CuRhO$_2$*

The activity of the copper sites in delafossite oxides has been investigated by choosing a B-sites whose coordination sphere is likely inert due to the closed-shell $d^0$ configuration. CuRhO$_2$ was chosen to investigate the ORR activity of a delafossite oxide with an open-shell, transition metal B-site. The first reported application of copper
delafossite oxides toward oxygen electrocatalysis focused on varying the B-site to study oxygen evolution reaction (OER) catalysis and found CuRhO$_2$ to have significantly high activity.$^{128,129}$ Demonstration of its ORR activity could provide motivation for use as a bifunctional catalyst. For simplicity, catalytic activity comparisons will be made to only CuLaO$_2$, due to the fact that the oxides tested up to this point have similar onset potentials, with CuLaO$_2$ having the highest electron transfer number.

The PXRD pattern of the CuRhO$_2$ is shown in Figure 30 and is consistent with the rhombohedral $R$-$3m$ polytype ($a = 3.075(1)$ Å, $c = 17.085$ Å). The $a$ lattice parameter and interatomic copper distance is noticeably smaller than the previously discussed Sc, Y, and La-based delafossite oxides.

![Indexed PXRD pattern of CuRhO$_2$ with calculated reference pattern (inset: SEM image of CuRhO$_2$ particles).](image)

Figure 30. Indexed PXRD pattern of $R$-$3m$ CuRhO$_2$ with calculated reference pattern (inset: SEM image of CuRhO$_2$ particles).
Cyclic voltammetry in argon-saturated 0.1 M KOH is again similar to previously tested cuprous delafossite oxides, indicating a pair of redox peaks likely due to the Cu$^{I}$/Cu$^{II}$ redox couple (Figure 31a). In the potential range of interest for ORR, the surface Cu$^{I}$/Cu$^{II}$ remain the only active redox couple. Figure 31b shows the typical capacitance-corrected ORR current densities at a rotation rate of 1600 rpm. CuLaO$_2$ and CuRhO$_2$ have nearly identical onset potentials and diffusion limited currents. The cyclic voltammetry and similar catalytic onset potentials again suggest that despite the structural and chemical changes, the active site surprisingly remains the same. The slight increase in diffusion limited current for CuRhO$_2$ could be due to the compound’s increased conductivity compared to the Cu(Sc,Y,La)O$_2$ series of delafossites.$^{9,128}$

Figure 31. (a) Cyclic voltammograms of CuLaO$_2$ and CuRhO$_2$ thin-film electrodes in argon-saturated 0.1 M KOH. (b) Linear sweep voltammograms in oxygen-saturated 0.1 M KOH (Rotation rate: 1600 rpm).
The Koutecky-Levich equation was applied to the catalyst RDE current densities at 100, 400, 900, and 1600 rpm. CuRh₂O₂ has electron transfer numbers in the range of \( n = 2.8-3.0 \), as shown in Figure 32a. Both oxides have similar calculated \( n \) values at each potential. Again, the fact that the activity of the carbon support is non-negligible in this potential region suggests the values solely due to the oxide active sites are likely higher. Figure 32b is the ORR Tafel plot for the catalysts using the kinetic currents derived from the Koutecky-Levich equation. The Tafel slopes are -56, and -58 mV dec⁻¹ for CuLaO₂ and CuRhO₂, respectively. These values are again close to the -59 mV dec⁻¹ typically attributed to a rate determining step involving migration of adsorbed oxygen intermediates.

Figure 32. (a) Electron transfer number (\( n \)) and (b) Tafel plots calculated from the Koutecky-Levich equation for RDE data of CuLaO₂, CuRhO₂, and the carbon black support. All potentials were \( iR \)-corrected. Error bars for electron transfer number represent at least three trials.
Interestingly, CuRhO₂ shows the highest electron transfer number out of the delafossite oxides tested and has similar onset potential. The cyclic voltammetry and onset potential support that copper is still the active site in catalysis. However, with the addition of the rhodium at the B-site, it cannot be ruled out that the copper-site is influenced electronically or even mechanistically by the neighboring rhodium octahedra. If conductivity was a significant factor in controlling the electron transfer number, CuLaO₂, which has the lowest conductivity, would not be expected to have the next highest values. On the other hand, the large interatomic copper distance of ~3.8 Å may explain the activity of CuLaO₂ by allowing for the potential bridging of oxygen species, but CuRhO₂ has the smallest copper distances of the oxides tested. Further investigation into the influence of the B-site is necessary to fully understand these catalytic activities.

**Delafossite Oxides for Oxygen Evolution Reaction**

Finally, the activity of CuLaO₂⁺ₓ and CuRhO₂ toward the oxygen evolution (OER) was briefly evaluated. As mentioned, the OER activities of several delafossite oxides, including CuYO₂ and CuRhO₂, were previously tested.¹²⁸,¹²⁹ The authors claimed activity was correlated to the B-site t₂g orbital occupancy, with CuYO₂ having the largest onset potential and CuRhO₂ the lowest. Figure 33 provides the OER responses of CuLaO₂⁺ₓ and CuRhO₂. The activity of CuRhO₂ was similar to literature reports. The low overpotential toward OER and high electron transfer number in ORR makes CuRhO₂ a promising candidate to further study for oxygen electrocatalysis. The activities of
CuLaO$_2$ and CuLaO$_{2+x}$ were again, surprisingly similar. The increased oxidation in does not appear to influence the ORR or OER activities.

Figure 33. Oxygen evolution response of CuLaO$_2$, CuLaO$_{2+x}$, and CuRhO$_2$ thin-film electrodes in oxygen-saturated 0.1M KOH. Forward and reverse scans were averaged to correct for capacitance. (Rotation rate: 1600 rpm).

5.4 Conclusion

In summary, the catalytic activities of the delafossite structured CuScO$_2$, CuYO$_2$, and CuLaO$_2$ towards ORR were investigated. The carbon-supported oxides showed improved onset potential, current, and electron transfer number over the bare carbon black, with CuLaO$_2$ having the highest prevalence of the complete four electron reduction of water. This supports the proposal of the bridging and dissociative mechanism of oxygen reduction by the larger interatomic copper distances.

The key factor limiting the catalytic activity of these delafossite oxides is likely the particle size and morphology of the solid state synthesized particles. The morphology
dependence of catalytic activity is well known for both metallic and some oxide
catalysts.\textsuperscript{123,125,135} Compared to the typical ABO$_3$ perovskite oxides reported for ORR, the
anisotropic layered delafossite structure makes particle morphology more central to the
catalytic performance. This is particularly important when copper is the proposed active
site. Under solid state synthetic conditions, the B-site octahedra-terminated (001) surface
is likely most stable.\textsuperscript{24} Even lower temperature hydrothermal methods have led to plate-
like particles with largely (001)-terminated surfaces.\textsuperscript{34,42} Considering this limitation, the
tested delafossite catalyst particles still show a similar ORR onset potentials to Cu$_2$O
nanoparticles relative to the carbon support.\textsuperscript{125} The catalytic current and calculated
electron transfer number though, may be limited by the morphology. Encouragingly,
recent developments in hydrothermal syntheses reported by our group show promise in
controlling delafossite morphology.\textsuperscript{42}

The capability of copper as a catalytic active site in delafossite electrocatalysts
was demonstrated. A wide range of the B-site cations exist to further influence the copper
site structurally or electronically. Appropriate transition metal B-sites, such as Mn$^{3+}$ or
Co$^{3+}$ widely used in perovskite oxides, could even become catalytically active sites
themselves. Considering the reported of delafossite B-site activity descriptors for OER
activity, one could also envision the potential for bifunctional catalysis by delafossite
oxides. Indeed CuRhO$_2$ showed enhanced electron transfer numbers toward ORR,
however, had a similar onset potential as the scandium, yttrium, and lanthanum based
delafossite oxides. Further work is necessary to fully characterize the active oxide
surfaces, especially if a potentially active B-site was used. Additionally, key to future
application of delafossite oxides in catalysis will be synthetic developments allowing for control of particle morphology. This study is hoped to further motivate investigation into the potential of the relatively unexplored delafossite family of oxides for oxygen electrocatalysis.
Chapter 6: Preliminary Investigation of Oxygen Reduction by CuLaO$_{2+x}$ for Low-Temperature Solid Oxide Fuel Cell Applications

6.1 Introduction

Chapters 4 and 5 introduced the oxygen reduction reaction (ORR) and proposed, as well as, demonstrated the use of delafossite oxides as heterogeneous ORR catalysts in alkaline solution. Motivation for that work came from the known oxidation and oxygen intercalation properties of delafossite oxides under mild conditions. The low temperature (250-450 °C) oxidation of CuScO$_2$ was investigated in Chapter 2, and the highly oxidized CuLaO$_{2+x}$ phase was prepared in Chapter 5. These interesting properties have also been studied in literature since the discovery of CuYO$_{2+x}$ and CuLaO$_{2+x}$ in 1993.$^{10,20-22,28,99-104}$ Typically, these studies involved structural characterization, thermogravimetric analysis, and properties measurements, such as electrical conductivity and magnetic susceptibility. In all, the oxidation properties are relatively understudied compared to the application of these compounds as p-type semiconductors in photovoltaics or photocatalysis. More recently, a Japanese group has published four papers investigating the so-called “oxygen storage capacity” of several delafossite oxides, comparing the results to cerium oxide, which is used in sensor and catalytic applications.$^{103,104,136,137}$ Taking the results presented in the previous chapters and literature into consideration, the potential of delafossite oxides in low temperature oxygen catalysis is intriguing.
Analogous to the alkaline ORR in alkaline fuel cells and metal air batteries discussed in Chapters 4 and 5, ORR occurs at the cathode of solid oxide fuel cells (SOFC) operated at elevated temperatures. Rather than reduction to an aqueous species, oxygen is reduced to the oxide ion at the cathode and transported through a solid electrolyte. Without a liquid electrolyte, cell performance is greatly dependent on the transport of oxygen species from the cathode to the cathode-electrolyte interface and ionic conductivity of each component. Intuitively, high temperatures are often needed to increase this transport of the oxygen species and oxide ions. Thus, the focus of much research has been to develop fuel cell components capable of operating efficiently at lower temperatures. Lower operating temperatures could allow for reduced costs by expanding compatible cell materials, reducing thermal insulation requirements, and improving tolerance to thermal cycling. However, as temperatures are lowered, the difficulty of the four-electron oxygen reduction reaction at the cathode becomes one of the dominating reasons for decreased cell performances. The rate limiting steps of ORR on current cathode materials are oxygen surface exchange and bulk/surface diffusion, which makes mixed electronic and ionic conducting oxides desirable.

Typically, reported SOFC cathodes are doped perovskite oxides. La$_{1-x}$Sr$_x$MnO$_3$ ($x=0.1\text{--}0.2$) (LSM) is widely used in high temperature SOFCs due its high electrical conductivity and compatibility with the common electrolyte material, yttria-stabilized zirconia (YSZ). However, it gains an oxygen excess at high temperatures, and exhibits poor ionic conductivity. La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ and La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ remain electronically conductive, but strontium substitution instead promotes oxygen vacancy formation and
the oxides become mixed conductors. However, these oxides can react to form insulating layers with a YSZ electrolyte.\textsuperscript{138,140}

The delafossite oxides have several properties making them appealing for use as SOFC electrodes. Concerning ORR itself, many of the similar arguments provided in Chapters 4 and 5 apply, namely the presence of reversible Cu\textsuperscript{I}/Cu\textsuperscript{II} sites and the ability to tune their interatomic distances. The insertion/removal of oxide at elevated temperatures without decomposition is also evidently possible from thermogravimetric studies and oxygen storage tests.\textsuperscript{21,104,127,141} However, the oxygen insertion can proceed in air up to only 450-500 °C before decomposition to oxidized, non-layered AB\textsubscript{2}O\textsubscript{4} or A\textsubscript{2}B\textsubscript{2}O\textsubscript{5} phases. State of the art “low temperature” SOFC components have minimum operating temperatures around 500 °C.\textsuperscript{138} Therefore, even though an active delafossite electrode below ~500 °C would be significant, realizing their full impact may require dramatic changes in cell materials and designs.

In this chapter, CuLaO\textsubscript{2+x} was tested as a cathode material for low temperature SOFCs. Based on previous alkaline ORR results and the known oxygen intercalation properties of CuLaO\textsubscript{2+x}, it was chosen to be the best candidate to investigate first. A stable low temperature phase was first characterized and its conductivity determined. Due to the literature and commercial prevalence of LSM cathodes on YSZ electrolytes, this system was used as a comparison for the CuLaO\textsubscript{2+x} cathodes. Symmetric cells using the different electrode materials were constructed and tested using electrochemical impedance spectroscopy.

80
6.2 Experimental

Materials. Copper (I) oxide (97%, Sigma-Aldrich), lanthanum (III) oxide (99.99% Alfa Aesar), lanthanum strontium manganite (LSM-20, ≥ 99%, Sigma-Aldrich), yttria-stabilized zirconia pellets (YSZ8-20, Fuelcellmaterials.com), Leitsilber 200 Silver Paint (Ted Pella, Inc), terpineol (anhydrous, Sigma-Aldrich), ethyl cellulose (Sigma-Aldrich), ethanol (200 proof, Decon Labs), de-ionized water (ρ = 18 MΩ•cm, Barnstead E-Pure), argon (99.998%, Praxair, Inc.), and oxygen (99.993%, Praxair, Inc.). Lanthanum (III) oxide was dried at 1000 °C immediately prior to use. All other materials were used without further purification.

Solid State Synthesis. Following previous literature reports, typical solid state syntheses of CuLaO$_2$ and CuLaO$_{2+x}$ were performed. CuLaO$_2$ was synthesized by heating of Cu$_2$O and La$_2$O$_3$ in an evacuated silica tube at 1050 °C for 72 hours.$^{22}$ CuLaO$_{2.66}$ is difficult to prepare without some stacking faults or the presence of additional less-oxidized phases. Regardless, the best reported synthesis involves heating CuLaO$_2$ at 280 °C for 4 days under flowing oxygen.$^{130}$

Characterization Methods. Products were characterized by powder X-ray diffraction (PXRD) with a Rigaku Corp. Geigerflex using Cu Kα$_1$ radiation. Thermogravimetric Analysis (TGA) (Q-500 thermogravimetric analyzer) was performed in flowing Ar or 5% H$_2$ (N$_2$ balance) at 5 °C min$^{-1}$.

Sample Preparation. For conductivity measurements, the desired powder was pressed into a 1.26 cm$^2$ by 0.1 cm thick pellet. Silver paint was applied to each side and dried at
120 °C. Platinum mesh pieces were attached using a small amount of silver paint to allow for connection to platinum wire.

Solid oxide fuel cell cathode tests required the assembly of symmetric cells with the desired powders as electrodes. Electrode pastes were prepared by mixing the electrode powder in a terpineol, ethyl cellulose, and acetic acid ethanolic paste. The pastes were then painted on either side of 19.90 mm diameter by 0.3 mm thick presintered yttria-stabilized zirconia (YSZ) pellets. A tape mask was used to set the electrode to a 12.5 mm diameter (A = 1.23 cm²). Lanthanum strontium manganite (LSM) electrodes were annealed at 1150 °C for 2 hours. CuLaO2+x (CLO) electrodes were annealed at 450 °C for 2 hours. All cells are denoted as Working Electrode/Electrolyte/Counter Electrode, for example, LSM/YSZ/LSM. After application of the working and counter electrodes on the YSZ electrolyte pellet, a small amount of silver paint was applied > 1 mm from the working electrode to act as the reference electrode. Platinum wire was attached to the reference electrode with small amount of silver paint.

_Elevated Temperature Electrochemistry._ For conductivity measurements, platinum wire was used to attach the sample pellet to the potentiostat (Gamry Reference 600). The pellet was then supported in a muffle furnace (Barnstead Thermolyne) for temperature control. The cell was allowed to equilibrate at each temperature for approximately 30 minutes. Electrochemical impedance spectroscopy measurements were performed with a frequency range of 0.1 Hz to 1 MHz, zero DC bias vs. open-circuit potential, and an AC
voltage amplitude of 10 mV. DC linear sweet measurements were also performed from 100 mV to -100 mV.

For solid oxide fuel cell symmetric cell tests, platinum mesh, attached to platinum wire, was press contacted to the working and counter electrodes using a custom fabricated ceramic holder. Platinum wire leads from the working, counter and reference electrodes were used to attach the cell to the potentiostat. The cell was then supported inside a muffle furnace (Barnstead Thermolyne) for temperature control. The cell was allowed to equilibrate at each temperature for approximately 30 minutes. More detail on the test setup is given in the following section. Electrochemical impedance spectroscopy measurements were performed with a frequency range of 0.1 Hz to 1 MHz, zero DC bias vs. open-circuit potential, and an AC voltage amplitude of 10 mV. The minimum frequency varied depending on sample. Select EIS data was analyzed using Gamry Echem Analyst software and the equivalent circuit shown in the text below. All electrochemical measurements were performed under ambient atmosphere and pressure.

6.3 Results and Discussion

**Stable Low-Temperature CuLaO$_{2+x}$ Phase**

CuLaO$_{2+x}$ has been characterized as the stoichiometric oxide (x = 0) and the highly oxidized phase (x > 0.5). A mixed phase likely exists at intermediate temperatures when heating CuLaO$_2$ in air, considering the oxidized phase undergoes slight structural changes. Structural changes could be undesirable in low temperature catalytic applications, as they could influence contact between particles or with s solid electrolyte.
In anticipation of thermal cycling involved in conductivity and SOFC cathode testing, a relatively stable low temperature phase must be characterized. First, to see the influence of temperature on the CuLaO$_2$ phase, the as synthesized oxide was subjected to similar heating and cooling that was used for later conductivity and SOFC tests (typically: from 100-450 °C in 50 °C increments, with approximately 30 minutes equilibration time at each temperature). Figure 34 shows the PXRD pattern of CuLaO$_2$ before and after heating. It is clear that significant structural changes occur after heating, with peaks from the original phase still present, but lowered in intensity. However, no peaks could be clearly assigned to the potential decomposition products Cu$_2$O, CuO, La$_2$O$_3$, or CuLa$_2$O$_4$. A mixture of varying oxidized phases are likely present with the likelihood of stacking faults between the possible polytypes and phases further complicating the pattern. Regardless, a complicated mixture such as this would make any future structural or stability characterization difficult.
To alleviate the formation of this complex mixture of CuLaO$_{2+x}$ phases, synthesis of a pure oxidized sample was attempted. As discussed before, pure CuLaO$_{2.66}$ is difficult to prepare but one of the best reported synthesis involves heating CuLaO$_2$ at 280 °C for 4 days under flowing oxygen. The pattern of the synthesized CuLaO$_{2+x}$ phase is shown in Figure 35 compared to the previous heated CuLaO$_2$ sample.

Figure 34. PXRD pattern of $R$-$3m$ CuLaO$_2$ before and after low temperature thermal cycling.
Figure 35. Comparison of PXRD patterns for CuLaO$_{2+x}$ and CuLaO$_2$ after low temperature thermal cycling.

It is clear that some peaks in the thermally cycled CuLaO$_2$ sample match those of the carefully oxidized CuLaO$_{2+x}$ phase, but still do not account for all the peaks. The synthesized CuLaO$_{2+x}$ matches closely to the idealized pattern of $P$-$31c$ CuLaO$_{2.66}$, as shown in Figure 36. The lattice parameters were calculated to be $a = 6.671(2)$ Å and $c = 10.382$ Å, consistent with literature.$^{127,130}$
Figure 36. Indexed PXRD pattern of $P\text{-}3\bar{1}c$ CuLaO$_{2+x}$ with calculated reference pattern.

The intentionally oxidized CuLaO$_{2+x}$ phase was then subjected to the same thermal cycling as before to see the impact of potential low temperature catalytic testing. Figure 37 shows the PXRD patterns the CuLaO$_{2+x}$ phase before and after heating. The structural changes before and after heating are significantly minimized compared to those of the unoxidized CuLaO$_2$. For the most part, low intensity peaks in the original pattern grow in intensity after heating. Again, these peaks are likely due to varying oxidized phases or stacking faults between polytypes, and no peaks can be assigned to possible decomposition products. Taking this into consideration, the CuLaO$_{2+x}$ phase was chosen for further characterization, conductivity measurements, and catalytic testing.
The oxygen content of the prepared CuLaO$_{2+x}$ was determined by reductive decomposition on heating in a reducing atmosphere (5 % H$_2$/95 % N$_2$) as shown in Figure 38. Decomposition to Cu + ½ La$_2$O$_3$ allowed for determination of the oxygen content to be CuLaO$_{2.63}$. The onset of decomposition and determined oxygen content are consistent with those reported in the first report of the CuLaO$_{2+x}$ phase.$^{127}$ Decomposition begins around 400-500 °C. Taking this into consideration, along with previous literature, 450 °C was chosen as the maximum temperature for annealing and testing of CuLaO$_{2.63}$. This sample was used for all further testing and for simplicity, and will be referred to as “CLO” for the SOFC half-cell tests.
Figure 38. Thermogravimetric analysis (TGA) of CuLaO$_{2+x}$ under inert (N$_2$) and reducing (5% H$_2$/95% N$_2$) atmospheres, indicating $x = 0.63$ (Heating rate = 5 °C min$^{-1}$).

*Low Temperature Conductivity of CuLaO$_{2+x}$*

Resistivity was measured on polycrystalline pellets of CuLaO$_2$ and CuLaO$_{2.63}$. Although the instability of the CuLaO$_2$ phase has been shown across this low temperature range, the results are included for comparison purposes. The calculated conductivities are shown in Figure 39a. The samples are semiconductors with CuLaO$_{2.63}$ having higher conductivities across all temperatures, as expected. The plot of ln($\sigma$) vs. 1/T in Figure 39b allowed for activation energy calculations of 0.38 eV and 0.29 eV for CuLaO$_2$ and CuLaO$_{2.63}$, respectively. The conductivities and activation energies are on the same order as previously reported. However, it is worth noting the conductivity of CuLaO$_{2.63}$ is several orders of magnitude lower than the common electronically conductive SOFC cathode material, La$_{0.8}$Sr$_{0.20}$MnO$_3$, across a similar temperature range.$^{143}$
Figure 39. (a) Temperature dependent conductivities and (b) corresponding Arrhenius plot of polycrystalline pellets of CuLaO$_2$ and CuLaO$_{2.63}$.

**Solid Oxide Fuel Cell Cathode Symmetric Cell Testing**

Many of the components for testing of SOFCs are commercially available, however, they are typically aimed towards full cell testing, which requires careful sealing between the anode and cathode, as well as gas flow control to each side. For the purposes of this study, where only the cathode is of concern, a symmetric cell setup was suitable. In this setup, both the working and counter electrodes are typical cathode materials, such as LSM, or the prepared CLO. To further minimize variables, the common solid electrolyte YSZ was purchased as presintered pellets from fuelcellmaterials.com. Unfortunately, no commercial sample holders exist to test SOFC symmetric cells, and descriptions of test setups in literature are often vague. For this reason, a custom holder was fabricated. The key requirements were that it must withstand elevated temperatures and provide good contact between the Pt mesh current collectors and the oxide electrodes. Figure 40 shows a representation of the developed sample holder. Two plates
of the machinable ceramic composite Macor® were separated by alumina tubes, with a third plate able to slide along the alumina tubes, using stainless steel springs to hold the sample in place against the top plate. The entire assembly was held together by high-temperature stainless steel wire fed through the alumina rods and top and bottom plates. This spring-loaded holder allowed for consistent contact between the Pt mesh current collectors and the electrodes during high temperature electrochemical testing.

Figure 40. SOFC cathode test setup, showing typical cell and custom sample holder.

Electrochemical impedance spectroscopy (EIS) is the most common method for evaluating electrode and cell performance in SOFCs. Each interface with an associated resistance and capacitive element is indicated by a semicircular feature in a Nyquist plot, as shown below. A Nyquist plot is the real impedance, equivalent to a resistor, as the x-axis and the imaginary impedance, arising from capacitive elements, as the y-axis. The frequency of an applied AC voltage is swept from high to low, leading to points on the
Nyquist plot going from left to right. The lowest frequency (rightmost) semicircular feature is often attributed to the charge transfer resistance directly related to ORR.\(^{144,145}\)

For the purposes of this investigation, the most important element of the Nyquist plots is the real impedance on the x-axis, which can provide the total resistance of the working electrode.

Even the current state-of-the-art low temperature SOFCs are still often tested at temperatures above the stability of delafossite oxides,\(^ {138}\) so control tests had to be performed with the commercial materials in the temperature range of interest. These tests were to be the first of any solid oxide fuel cell component tests performed in the Wu group, so they also served to confirm the test setup and cell fabrication were adequate. First, the simplest symmetric cell was fabricated. LSM electrodes were painted onto each side of a YSZ electrolyte pellet and annealed at 1150 °C for 2 hours. The temperature was increased from room temperature to 600 °C in 50 °C increments. At each temperature the cell was allowed to equilibrate for at least 30 minutes before EIS was performed. Figure 41 shows the Nyquist plots from 400-600 °C of the LSM/YSZ/LSM cell. Below 400 °C, no clear spectra could be obtained. The Nyquist plots are dominated by a single feature. Due to the high electrical conductivity of the LSM, resistance at interface with the current collector is minimized. In addition, the relatively low surface area in contact with the YSZ, also leads to a low resistance. Therefore, the feature can be attributed to ORR at the LSM working electrode. The resistance of this process decreased with increasing temperature. The small, unresolved high frequency feature at low temperature could be due to the influence of the decreased LSM conductivity at low
temperature at one of the interfaces. Worth noting is that the resistance of the electrode at 450 °C, roughly the maximum temperature for CLO, is around 200 Ω.

Figure 41. Nyquist plots of LSM/YSZ/LSM symmetric cell at 400-600 °C in air.

A similar symmetric cell was then fabricated, but with the CLO material as the electrodes on the YSZ electrolyte. For electrodes with CLO, the maximum annealing and test temperature was chosen as 450 °C, due to the stability of the phase. Figure 42 shows the Nyquist plots from 150-400 °C of the CLO/YSZ/CLO cell. Interestingly, an EIS response was able to be measured at much lower temperatures than the LSM symmetric cell. However, compared to the LSM cell, no clear features can be observed, and the responses are clearly no longer dominated by a single interface. Also, the total resistances of the responses are several orders of magnitude greater than the LSM cell (at 450 °C, ~200 Ω for the LSM cell compared to the ~800 kΩ for the CLO cell). When using a three-electrode cell, such as these cells with a silver paste reference electrode, there is an assumption that the counter electrode is not limiting the current of the cell. In other words, the current generated at the working electrode must be able to be matched by the
counter electrode. In the case of CLO, because the resistances are obviously much higher, a CLO counter electrode is like limiting and not allowing for a true measurement at the working electrode. LSM has a much higher conductivity near 400-450 °C, the maximum of CLO cell operation, so cells were assembled with a CLO working electrode and LSM counter electrode.

Figure 42. Nyquist plots of CLO/YSZ/CLO symmetric cell at 150-450 °C in air.

Figure 43 provides the Nyquist plots for a CLO working electrode with an LSM counter electrode. The total resistances are significantly reduced across all temperatures compared to the CLO/YSZ/CLO cell, indicating that the CLO counter electrode was likely limiting in the latter. The resistance is several orders of magnitude lower at 450 °C: ~3 kΩ for the CLO/YSZ/LSM cell compared to the ~300 kΩ for the symmetric CLO cell. Still, no clear features can be observed, making determination of the exact resistance and capacitance values difficult.
Figure 43. Nyquist plots of CLO/YSZ/LSM cell at 250-450 °C in air.

A more accurate measurement of the CLO working electrode was obtained, but the resistance is still much greater than the commercial LSM electrode. Even at 450 °C, well below the typical operating temperature of LSM-based SOFCs, the resistance is ~15 Ω for the LSM/YSZ/LSM cell compared to ~3000 Ω when the working electrode is changed to CLO. The Nyquist plot comparing these two cells is shown in Figure 44.

Figure 44. Nyquist plot comparing LSM and CLO working electrodes on YSZ at 450 °C in air.
In order to better elucidate the relative performances of the LSM and CLO electrodes, SEM imaging of the cell cross-sections was performed. Figure 45 shows the LSM/YSZ and CLO/YSZ interfaces. Most obvious is the difference in particle size of the two oxides. The larger particles of the CLO powder limits minimum thickness of electrode that can be applied uniformly. A thicker electrode can limit any oxide conduction within or on the surface of the catalyst, lowering activity. In addition, the large particles and thicker films severely limit the triple-phase boundary, where the electrolyte, electrode, and oxygen are all in contact allowing for reduction of oxygen and direct formation of oxide within the conductive electrolyte. The LSM electrode clearly has a more porous structure with pathways for oxygen to reach the LSM/YSZ interface.

![Figure 45. Cross-section SEM images of LSM/YSZ and CLO/YSZ interfaces.](image)

For electronically conductive cathode materials, such as LSM, one way of improving performance is mixing the cathode powder with the electrolyte powder to increase the active triple phase boundary area where oxygen can be reduced to oxide by the cathode and transported by the ionically conductive electrolyte.\textsuperscript{144,145} To first confirm the positive influence of this, LSM was mixed with the YSZ powder in a 1:1 weight ratio
and applied as the working and counter electrode and annealed at 1100 °C for 2 hours. To ensure good electrical contact with the current collectors, a thin layer of pure LSM was also applied on top of the LSM-YSZ composite. Figure 46 compares the LSM and LSM-YSZ composite electrodes at 400, 450, and 600 °C.

Figure 46. Nyquist plots comparing LSM and LSM-YSZ composite working electrodes at 400-600 °C in air.

Though difficult to clearly see, the addition of YSZ in the electrode added an additional high frequency (leftmost) feature. When the LSM and YSZ are more intimately mixed, with greater surface area of contact, the interfacial resistance becomes more significant. The defined features of the Nyquist plots for these LSM-based cells makes fitting of the EIS spectra possible. An equivalent electrical circuit can be modeled after the cell, as shown in Figure 47. The initial resistance $R_1$ includes the uncompensated resistance between the reference and working electrodes, the contact resistance between the working electrode and Pt current collectors, and the resistance of the leads. $R_2$ in parallel with the constant phase element $CPE_2$ accounts for the high frequency features typically
due to working electrode-electrolyte interfaces. The final $R_3$ in parallel with the constant phase element $CPE_3$ accounts for the low frequency feature associated with the charge transfer of the ORR reaction, as mentioned previously.\(^\text{144}\)

![Equivalent circuit model for LSM and LSM-YSZ symmetric cells with fitted values from 450-600 °C.](image)

<table>
<thead>
<tr>
<th>LSM/YSZ/LSM</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
<th>$CPE_2$ (S⁻¹)</th>
<th>$n_2$</th>
<th>$R_3$ (Ω)</th>
<th>$CPE_3$ (S⁻¹)</th>
<th>$n_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 °C</td>
<td>52.1(4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>195(3)</td>
<td>0.00085(3)</td>
<td>0.73(1)</td>
</tr>
<tr>
<td>500 °C</td>
<td>23.8(2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>78(1)</td>
<td>0.00130(6)</td>
<td>0.73(1)</td>
</tr>
<tr>
<td>550 °C</td>
<td>14.8(1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>31.1(5)</td>
<td>0.0019(1)</td>
<td>0.74(1)</td>
</tr>
<tr>
<td>600 °C</td>
<td>10.1(1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.5(2)</td>
<td>0.0030(4)</td>
<td>0.75(2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>LSM/YSZ/YSZ/LSMZ</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
<th>$CPE_2$ (S⁻¹)</th>
<th>$n_2$</th>
<th>$R_3$ (Ω)</th>
<th>$CPE_3$ (S⁻¹)</th>
<th>$n_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 °C</td>
<td>30.9(8)</td>
<td>4.1(8)</td>
<td>0.004(2)</td>
<td>0.75(1)</td>
<td>11.4(9)</td>
<td>0.0117(4)</td>
<td>0.74(2)</td>
</tr>
<tr>
<td>500 °C</td>
<td>11.4(2)</td>
<td>1.7(3)</td>
<td>0.004(1)</td>
<td>0.75(1)</td>
<td>30.0(1)</td>
<td>0.0164(5)</td>
<td>0.77(3)</td>
</tr>
<tr>
<td>550 °C</td>
<td>6.50(7)</td>
<td>0.8(2)</td>
<td>0.007(3)</td>
<td>0.75(1)</td>
<td>16.2(7)</td>
<td>0.025(1)</td>
<td>0.77(3)</td>
</tr>
<tr>
<td>600 °C</td>
<td>4.24(1)</td>
<td>0.5(1)</td>
<td>0.008(3)</td>
<td>0.75(1)</td>
<td>6.4(3)</td>
<td>0.031(2)</td>
<td>0.81(3)</td>
</tr>
</tbody>
</table>

Figure 47. Equivalent circuit model for LSM and LSM-YSZ symmetric cells with fitted values from 450-600 °C.

Comparing the fitted circuit values for the LSM and LSM-YSZ symmetric cells, it is clear the addition of the YSZ in the electrode lowers resistance across the temperature range. These values also allow for a more accurate comparison to literature, further demonstrating the cell fabrication and the developed test setup are adequate.

A similar YSZ composite electrode was prepared for the CLO cathode in attempts to improve performance. Unfortunately, the composite electrode greatly increased the electrode resistance compared to the pure CLO electrode, as shown in Figure 48. One possible explanation for this poor contact between the CLO and YSZ materials, and
mixing the two the increases surface area in contact, thereby increasing the associated resistance.

Figure 48. Nyquist plots comparing CLO and CLO-YSZ composite working electrodes at 450 °C in air.

Poor contact between the CLO and YSZ electrolyte is reasonable considering the difference in annealing temperatures during cell fabrication between the LSM and CLO cells. Due to stability of the CLO, the maximum annealing and operation temperature is around 450 °C. The LSM electrode can be annealed at much higher temperatures, ensuring good contact between not only the LSM and YSZ, but between LSM particles within the electrode. High fabrication temperatures are used for this reason, even if the cell is to be operated at lower temperatures. The more complicated Nyquist plots for the CLO cells also make sense considering this possible influence of the annealing temperature. There are likely several more resistive interfaces in the CLO cells due to poor electrical contact.
Considering these factors, comparison of the LSM/YSZ/LSM cell, with a 1150 °C annealed working electrode, and the CLO/YSZ/LSM cell with a 450 °C annealed working electrode, is likely not fair. In attempts to have a better comparison, a cell was prepared with an LSM working electrode annealed at 450 °C. The Nyquist plots of this cell, denoted as LSM450/YSZ/LSM, are shown in Figure 49.

Figure 49. Nyquist plots of LSM450/YSZ/LSM cell at 400-450 °C in air. LSM450 indicates the LSM electrode annealed at only 450 °C prior to testing.

No clear spectra could be obtained below 400 °C. In the range of 400-450 °C, the resistances increase by nearly an order of magnitude compared to the previous LSM/YSZ/LSM cell. Similar to the CLO cells, the Nyquist plots become more complex, with no clear model able to be fit to the data. Figure 50 compares the LSM and CLO cathodes, now both annealed at 450 °C. The two electrodes at least now have resistances on roughly the order of magnitude. However, the LSM cathode is clearly still at a much lower resistance.
To date, Figure 50 provides the best comparison of CLO to the commercial LSM. Unfortunately, even after lowering the annealing temperature of the LSM cathode, it still outperforms CLO. However, this comparison is far from ideal. The fabrication process of the CLO cathode needs to be improved so that there is no doubt in its contact with the electrolyte. The next section provides some insight into the potential directions to improve on these results.

6.4 Conclusion and Future Directions

This chapter presented the preliminary investigation of low temperature oxygen reduction by the oxidized delafossite CuLaO$_{2.63}$. The precedent for oxygen intercalation/deintercalation within the copper layer of delafossite oxides motivated this study. Oxygen reduction and release is obviously thermodynamically favorable at these
low temperatures, and vacancies within the intercalated oxygen layer could potentially allow for oxide conductivity. Unfortunately, the immaturity of the Wu lab in this field slowed and limited the scope of these initial investigations. Additionally, low temperature solid oxide fuel cell materials are only the focus of academic research, making comparison to state of the art materials difficult. Current high performance cathodes and electrolyte materials can have complicated chemical compositions or fabrication methods. For this reason, commercially available LSM and YSZ materials were chosen for these initial tests. Regardless of these limitations, some encouraging conclusions can be made. In particular, the CLO electrodes showed promising responses at extremely low temperatures (< 400 °C). Figure 51 shows the Nyquist plots of LSM and CLO symmetric cells and the CLO/YSZ/LSM cell at 300 and 350 °C. The lowered resistances of the CLO electrode are obvious at these temperature. The LSM symmetric cell appears to possibly be just noise, however, the data passed the Kramers-Kronig test and intersections of two features can be seen in the inset. Each of these features clearly much larger resistances at each temperature. In this temperature range and lower, even the CLO symmetric cell has lower resistances, whereas the LSM cell has immeasurably high resistance or noise below 300 °C.
Figure 51. Nyquist plots comparing LSM/YSZ/LSM, CLO/YSZ/CLO, and CLO/YSZ/LSM cells at 300 and 350 °C in air.

Although the application of CuLaO$_{2.63}$ and other delafossite oxides as solid oxide fuel cell electrodes for power generation may still be unclear, the course of this investigation brought to light another potential application. The interesting oxidation properties of delafossite oxides could also be utilized in elevated temperature catalytic reactions, such as the oxidative dehydrogenation of alkanes. Like oxygen reduction, oxidative dehydrogenation involves adsorption and dissociation of oxygen, but the oxygen species then abstract hydrogen from small alkanes to produce industrially relevant alkenes, such as ethylene and propylene.$^{147,148}$ The intercalated oxygen in the delafossite structure could, with the appropriate choice of interatomic copper distances, provide additional control in these reactions, limiting combustion products and increasing selectivity. Preliminary testing is currently in progress.
Chapter 7: Conclusions

Cuprous delafossite oxides are a family of complex oxides uniquely structured with alternating layers of linearly coordinated O-Cu\textsuperscript{I}-O and M\textsuperscript{III}O\textsubscript{6} edge-shared octahedra. This structure is responsible for several interesting properties, such as p-type conductivity through a delocalized Cu 3\textit{d} and O 2\textit{p} orbital valence band, susceptibility to both extrinsic acceptor doping and oxygen intercalation within the copper layer, and high optical transparency. However, reported applications of these oxides have been relatively limited, especially compared to perovskite structured oxides. One reason for this is likely the difficulties faced controlling morphology, impurities, and doping in their syntheses. The same attributes that make delafossite oxides appealing such as their anisotropic layered structure and low coordination copper sites, introduce several synthetic problems.

The work presented here started with this synthetic challenge, first focusing on the synthetic chemistry in understanding the phase formation and crystallization of CuScO\textsubscript{2}, then from the observed properties of CuScO\textsubscript{2}, the potential application of delafossite oxide as oxygen electrocatalysts was proposed and investigated.

The initial project reported in Chapter 2 led to the first reported low temperature hydrothermal synthesis of the delafossite CuScO\textsubscript{2}, a potential p-type transparent conducting oxide. The properties of CuScO\textsubscript{2} lead to several synthetic challenges. Significant oxygen intercalation within copper layer means control of oxidation proves
difficult by the conventional solid state syntheses. Often syntheses require careful control of temperature and atmosphere, or intentional doping. Through consideration of copper and scandium species hydrolysis, the first hydrothermally synthesized pure CuScO$_2$ was reported. The following chapter investigated the influence of oxygen intercalation on the optical and photoelectrochemical properties of the hydrothermally synthesized CuScO$_2$. Post annealing treatments were found to increase copper oxidation, leading to increased light absorption, and shift the flat band potential due to increased hole carrier density. The oxide was then applied as a p-type semiconductor in p-type dye sensitized solar cells.

The observed oxygen intercalation in CuScO$_2$ led to an original research proposal and subsequent demonstration of cuprous delafossite oxides for heterogeneous oxygen electrocatalysis in Chapters 4 and 5. The delafossite structure possesses several key elements that could potentially make it desirable for catalytic applications: the presence of low-coordination Cu-sites, which are accessible by O$_2$ molecules, and the ability to alter lattice space around Cu-sites by changing the size of the M$^{III}$ cation. The series of oxides CuMO$_2$ (M = Sc, Y, La) where chosen to provide a range of Cu-Cu spacing from ~3.2-3.8 Å. The alkaline oxygen reduction activity was monitored by rotating-disk electrode electrochemistry in aqueous alkaline solutions. The oxides were found to have improved onset potential relative to the carbon support, and CuLaO$_2$ had the highest prevalence of the complete four electron reduction of O$_2$.

Finally, Chapter 6 presented initial studies performed on the use of CuLaO$_2$ as a potential low temperature solid oxide fuel cell cathode material for the oxygen reduction reaction. To study the low temperature oxygen reduction activity of CuLaO$_2$, a custom
solid oxide fuel cell half-cell holder was first designed and fabricated. Electrochemical impedance spectroscopy was then used to compare the oxide to a widely-used, commercially available cathode material.

The focus on individual copper and scandium species hydrolysis led to the first reported phase-pure CuScO$_2$ hydrothermal synthesis. The presented rationale is unique compared to other reported complex oxide hydrothermal syntheses, namely, a low pH was used rather than concentrated base to prevent insoluble oxide/hydroxide formation. Even though the work focused solely on phase formation, a viable hydrothermal synthesis opens up possibilities for morphology control through addition of surfactants or fine tuning of reaction conditions. In addition the synthetic rationale can be applied to other delafossite oxides, as has been done already with CuGaO$_2$ in the Wu group. The solubility of scandium species give hope that yttrium or lanthanum-based cuprous delafossite oxides could be synthesized under similar conditions.

The first demonstration of cuprous delafossite oxides as alkaline oxygen reduction catalysts shows the potential for the tunable copper sites in a variety electrocatalytic processes involving oxygen species. The results and the proposed use of these oxides hopefully motivates more research on their synthesis as outlined above. Control of the exposed surfaces can likely have a significant impact on catalytic performances, particularly when copper is the proposed active site. Lastly, the preliminary investigation of low temperature oxygen electrocatalysis provides a starting point for exciting new applications involving oxidation at low temperatures, such as the industrially relevant oxidative dehydrogenation reaction of alkanes.
References


(30) Zhao, Q.; Zhao, X.; Sleight, A. W.; Li, J. International Society for Optics and Photonics, 2003; pp 248–253.


(36) Laugier, J.; Bochu, B. 3rd ed. CELREF.


(60) Yu, M.; Draskovic, T. I.; Wu, Y. *Phys. Chem. Chem. Phys.* 2014, **16** (11), 5026.


(80) Schimpf, S.; Bron, M. In Fuel Cell Science and Engineering; Stolten, D., Emonts, 111


